

SOLID SOLUBILITY AND RESIDUAL RESISTIVITY OF SCANDIUM IN ALUMINUM

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Summary

The solid solubility and the residual resistivity of Sc in Al were determined by means of the measurement of the electrical resistivity at 77 K of Al-Sc alloys air cooled after annealing at various temperatures for a time sufficient to complete the precipitation of the equilibrium phase (ScAl_3). Moreover, the solidus line of the Al-rich alloys was determined by thermal analysis. The solid solubilities of Sc in Al were found to vary from 0.186 at.% at 913 K to 0.033 at.% at 743 K. From the temperature dependence of the solid solubility the excess entropy of mixing Δs and the heat of mixing Δh associated with the solid solution of Sc in Al were calculated to be 6.0 R and 59 kJ mol⁻¹, respectively. The compound ScAl_3 reacts eutectically with Al to form an Al-rich solid solution. The eutectic temperature is 823 ± 1 K. Using the values of Δs and Δh , the maximum solid solubility of Sc in Al was estimated as 0.21 at.% at the eutectic temperature. The resistivity increment caused by Sc atoms in solution is linearly proportional to the concentration of Sc. The residual resistivity for Sc in Al is $(3.4 \pm 0.1) \times 10^{-8} \Omega \text{ m (at.\%)}^{-1}$.

1. Introduction

It is well known that a small amount of a transition metal exerts a pronounced influence on the structure and properties of Al and Al alloys. Information about the Al-rich side of the phase diagram is relevant to an understanding of the behavior of the transition metals in Al and Al alloys, and the residual resistivities of the transition metals in Al are related to the electronic structure of the Al-rich solid solution. Reliable measurements of the solid solubility and the residual resistivity of Sc in Al have not been reported;

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there is also a controversy about whether the Al-rich side of the Al–Sc system is of a eutectic or peritectic type [1].

In the present work the solid solubility and the residual resistivity of Sc in Al were investigated by the measurement of electrical resistivity at 77 K. The solidus line of the Al-rich side of the system was determined by thermal analysis.

2. Experimental

2.1. Zone refining of aluminum

Al ingots (99.999 wt.%) supplied by Sumitomo Chemical Co. Ltd. were zone refined to avoid the influence of impurity atoms on the solid solubility and the residual resistivity of Sc in Al. The starting material was rolled and cut to a square rod $1 \times 1 \text{ cm}^2$ in cross section and 25 cm long. After the machining, the surface of the rod was polished chemically in a 3:1 mixture of H_3PO_4 and HNO_3 at 363 K. The rod was set in a high purity graphite boat and placed in a quartz tube. It was melted with induction heating in a vacuum of better than 10^{-1} Pa. The conditions for the zone refining were as follows: zone speed, 13 cm h^{-1} ; zone length, 2 cm; number of passes, 10. The surface of the rod was polished chemically in the solution at 363 K after each pass. A 5 cm length of the tail of the zone-refined Al was removed after every five passes and the remainder was used for the preparation of specimens.

2.2. Preparation of Al–Sc alloys

The Al–Sc master alloys containing 1.81 and 6.85 at.% Sc were prepared by melting the high purity Al in a high purity graphite crucible and then adding 99.9 wt.% Sc wrapped in high purity Al foil in an atmosphere of pure argon. The melt was thoroughly stirred before pouring and was cast into a preheated iron mould. Al–Sc alloys of the desired compositions were prepared by dilution of the master alloys with high purity Al using the method of zone refining. The whole of the specimen, 6 cm in length, was then kept molten for a time sufficient to homogenize the Sc distribution. The alloys were rapidly solidified. Zone levelling was not carried out because the distribution coefficient of Sc in Al is nearly equal to 1. The ingots were homogenized at 873 K for 10 d and formed into wires 0.6 mm in diameter by cold swaging and drawing.

2.3. Analyses of composition

The concentration of Sc in the alloys was determined mainly by flame spectrochemical analysis and, for comparison, by photon activation analysis. Table 1 shows the method of analysis and the precision of the flame spectrochemical analysis used in the present work.

The photon activation analysis was carried out by bremsstrahlung irradiation using the linear electron accelerator at Tohoku University. The

TABLE 1

Analysis method of Sc concentration in Al-Sc alloy and analysis precision by means of flame spectrochemical analysis

(1) Analysis method

Sample 0.2 g
 ↓ + 5 mg Fe³⁺
 + 20 ml 20% NaOH
 Decomposition by heating
 ↓
 Filtration
 ↓ + HCl
 Dissolution of precipitates
 ↓ + H₂O
 Dilution in volumetric flask (100 ml)
 ↓
 Flame spectrochemical analysis
 (Flame C₂H₂-air; wavelength 604 nm)

(2) Analysis precision

Reproducibility ($n = 5$) using standard solution

Arithmetic mean (\bar{x}) = 4.89 mg Sc

Range (R) = 0.15

Standard deviation ($\hat{\sigma} = R/d_2$) = 0.065

Relative standard deviation ($= \hat{\sigma}/\bar{x}$) = 1.32%

specimens of Al and the Al-Sc alloys were small plates $4 \times 8 \times 0.2$ mm³. A small amount of 99.9 wt.% Sc was used as a standard. In order to monitor the bremsstrahlung flux, accurately weighed plates of Au, 0.1 mm thick, were placed on the front and back of each specimen and irradiated together with the specimens. Each specimen was wrapped in Al foil. The ¹⁹⁶Au activities produced by the ¹⁹⁷Au(γ, n)¹⁹⁶Au process were used for comparison. A mean specific activity was used to determine the dose rate of bremsstrahlung to which the specimen was exposed. The specimens and the Au monitors were encapsulated in a quartz tube and this unit was placed in a water-cooled specimen holder on the bremsstrahlung beam axis behind the photon-producing converter. The average beam current was measured at the converter using a current monitor. The irradiation conditions were as follows: electron energy, 30 MeV; γ -ray dose rate, about 1.3×10^3 C kg⁻¹ at the sample position; time of irradiation, 2 h. The γ -ray spectra were measured 6 d after the irradiation, using an Li-drifted Ge detector with a sensitive volume of 24 cm³ and a 1024-channel pulse height analyser. Figure 1 shows typical γ -ray spectra of the irradiated Al-Sc alloy and the Au monitor. Values on each peak are energies in MeV. Characterization of the γ -rays was obtained from a knowledge of the γ -ray spectra of a standard source (⁵⁷Co, ⁵⁴Mn, ²²Na, ⁶⁰Co, ¹³⁷Cs, ⁸⁸Y and ²⁰³Hg) and nuclear data [2]. The concentration of Sc in the Al-Sc alloys was calculated using the 0.271 MeV peak of ^{44m}Sc pro-

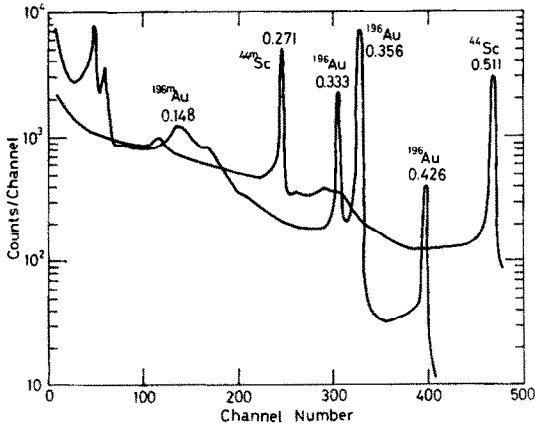


Fig. 1. Gamma-ray spectra of an Al-Sc alloy and the Au monitor irradiated by bremsstrahlung.

TABLE 2

Chemical composition of specimens

Specimen No.	Flame spectrochemical analysis (at.%)	Photon activation analysis (at.%)
1	0.014	0.02
2	0.016	—
3	0.023	—
4	0.036	—
5	0.037	—
6	0.038	0.04
7	0.066	—
8	0.068	—
9	0.079	—
10	0.088	—
11	0.113	—
12	0.134	0.14
13	0.160	—
14	0.186	—
15	0.198	—
16	1.81	1.9
17	6.85	6.0

duced by the (γ, n) reaction. The results are shown in Table 2; the values obtained by activation analysis are in good agreement with those from flame spectrochemical analysis. The flame spectrochemical analyses were used to determine the solid solubility, the residual resistivity and the solidus temperature.

2.4. Electrical resistivity measurement and thermal treatment

Electrical resistivity was measured in wires 0.6 mm in diameter and 60 cm long. The specimen for the electrical resistivity measurement was mounted on a quartz support.

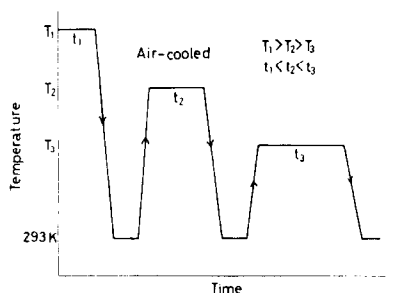


Fig. 2. Schematic diagram of the heat treatment used in the present work.

In determining the solid solubility of Sc in Al, much care was expended upon the following aspects of the thermal treatment.

(1) The precipitation of the equilibrium phase (ScAl_3) must be completed at various temperatures, bearing in mind that the diffusion of transition metals in Al is generally slower than the self-diffusion of Al.

(2) The concentration of quenched-in vacancies must be reduced as much as possible, because the solid solubility of Sc in Al is assumed to be small and therefore the contribution of quenched-in vacancies to the electrical resistivity cannot be neglected.

In the present work, the thermal treatment was carried out continuously using the method shown in Fig. 2. Each specimen was used repeatedly to obtain data at various temperatures, *i.e.* specimens were replaced in a horizontal electric furnace after each measurement was carried out. After annealing at various temperatures for a time sufficient to complete the precipitation of the ScAl_3 phase, the specimen was air cooled. Following immersion in acetone at 273K , the specimen was immediately immersed in liquid nitrogen. The time between the air cooling and the immersion in the liquid nitrogen bath was about 20 s . This cooling process is slow enough to prevent the production of quenched-in vacancies, but fast enough to retain the supersaturated solid solution. The specimens were annealed at the following temperatures: 923 K (3 h), 913 K (4 h), 903 K (5 h), 893 K (7 h), 873 K (10 h), 863 K (15 h), 853 K (20 h), 833 K (25 h), 813 K (39 h), 793 K (45 h), 773 K (65 h) and 743 K (72 h). The high purity Al was annealed for 10 min at each of the following temperatures and then air cooled: 903 , 873 , 823 , 773 , 723 and 673 K . The measurement of electrical resistivity was carried out at liquid nitrogen temperature using a precision potentiometer. Correction for the liquid nitrogen temperature was made with a dummy specimen. Both ends of the specimen itself were used as current leads. High purity Al wires 0.6 mm in diameter were spot-welded to the specimen as potential leads. The distance between the potential leads on the specimen was about 30 cm . After the measurement the diameter of the specimen and the distance between the potential leads were measured and the specific electrical resistivity was calculated.

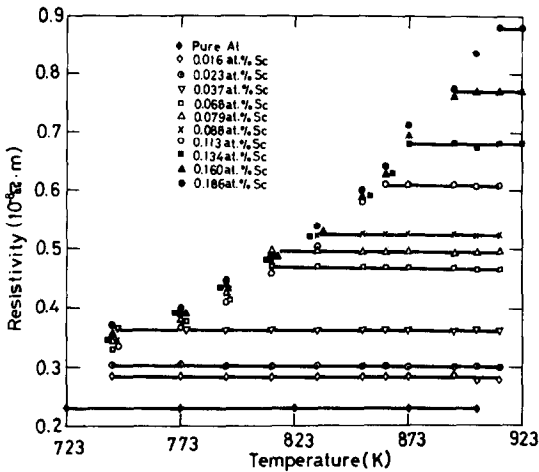


Fig. 3. Resistivity of Al-Sc alloys vs. annealing temperature for various Sc concentrations.

2.5. Thermal analysis

A Chromel-Alumel thermocouple was wrapped with the Al-Sc alloy wire and put into a protective tube. The thermocouple was connected to an X-Y recorder. An electric furnace was heated or cooled at $\pm 1.5 \text{ K h}^{-1}$ using a regulator with a programming function. The solvus temperature was determined from the temperature of the exothermic or endothermic plateau which appeared in the heating or cooling curve owing to the fusion or solidification. The thermoelectric power of the thermocouple was checked using the values of the freezing point and melting point of the 99.999 wt.% Al.

3. Results

Figure 3 shows the resistivities for high purity Al and for the Al-Sc alloys as a function of annealing temperature. The resistivity of the high purity Al is constant over all annealing temperatures, indicating that quenched-in vacancies were not introduced by air cooling. The resistivity curve of the Al-Sc alloy consists of an increasing region and a constant region. The increasing part of the curve is caused by the increase in solid solubility with rising temperature. All the scandium is in solution above a certain temperature and the resistivity remains constant when the specimen is subjected to further annealing at higher temperatures. Figure 4 shows the resistivity as a function of the concentration of Sc at various temperatures; the break in the curve was regarded as the solubility limit. The solid solubilities determined in this way are shown in Table 3.

Generally, for a sufficiently dilute solid solution the variation of the solid solubility with temperature is given by

$$C = e^{\Delta s/R} e^{-\Delta h/RT} \quad (1)$$

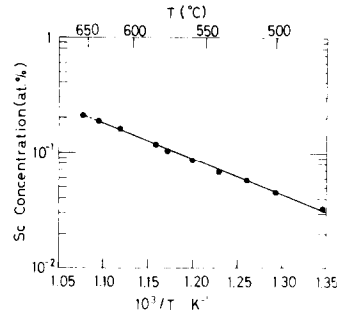
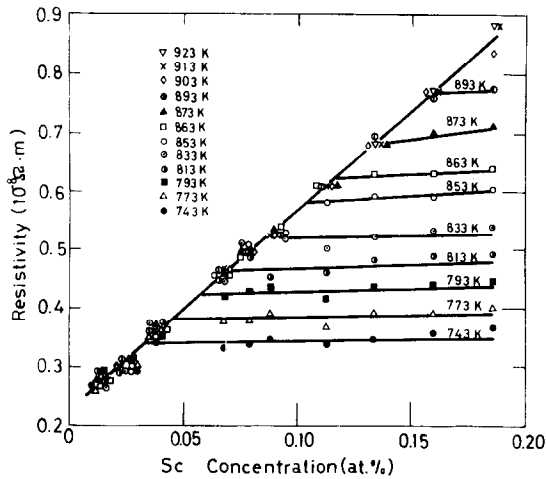


Fig. 4. Resistivity of Al-Sc alloys vs. Sc concentration for various annealing temperatures.

Fig. 5. Temperature dependence of the solid solubility of Sc in Al.

TABLE 3

Solid solubility of Sc in Al

Temperature (K)	Sc concentration (at.%)
913	0.186
893	0.160
873	0.134
863	0.117
853	0.104
833	0.086
813	0.068
793	0.058
773	0.045
743	0.033

where C is the solid solubility in atomic per cent, Δs the excess entropy of mixing, R the gas constant, Δh the heat of mixing and T the temperature (in kelvins). Figure 5 shows the logarithm of the solid solubility of Sc in Al as a function of the reciprocal temperature. The results are satisfactorily expressed by eqn. (1) and the calculated values of Δs and Δh are shown in Table 4, with those [3] of other 3d transition metals.

The solubility line and the solidus line are shown in the phase diagram of Fig. 6, together with the results of Mondolfo [1]. Figure 6 shows that the compound ScAl_3 reacts eutectically with Al to form an Al-rich solid solution. The concentration dependence of the solidus temperature is very small. The eutectic temperature is estimated to be equal to (823 ± 1) K, in good agreement with Mondolfo [1]. The maximum solid solubility of Sc in Al was calculated from Δs and Δh to be 0.21 at.% at the eutectic temperature.

TABLE 4

Maximum solid solubility C_{\max} , excess entropy of mixing Δs and heat of mixing Δh for 3d transition metals in Al

Element	C_{\max} (at.%)	$\Delta s/R$	Δh (kJ mol ⁻¹)
Sc	0.21	6.0	59
Ti	0.57	2.6	60
V	0.32	—	—
Cr	0.44	0.46	47
Mn	0.9	3.8	67
Fe	0.025	2.3	82
Co	0.009	—	—
Ni	0.018	7.6	125
Cu	2.5	1.8	39

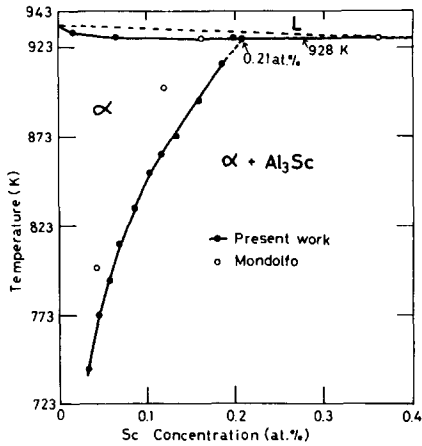


Fig. 6. The Al-rich side of the equilibrium phase diagram of the Al-Sc system as determined in the present work, in comparison with the results of Mondolfo [8].

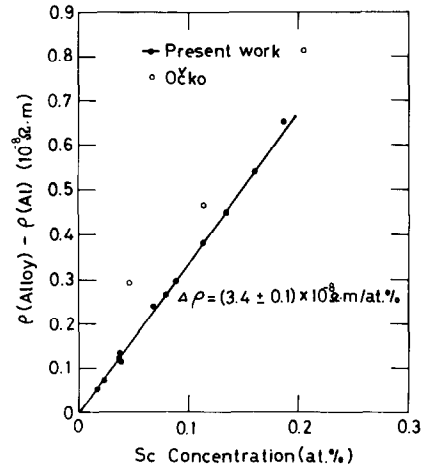


Fig. 7. The resistivity increment of Al-Sc alloys as a function of the Sc concentration in solid solution.

Figure 7 shows the concentration dependence of the difference between the resistivities of the constant parts for the Al-Sc alloy and the high purity Al in Fig. 3, along with the data of Ocko [4]. From the result, the residual resistivity per atomic per cent of Sc in Al is found to be $(3.4 \pm 0.1) \times 10^{-8} \Omega \text{ m (at.\%)}^{-1}$.

4. Discussion

4.1. Method of determination of the solid solubility of Sc in Al

Figure 4 shows that the resistivity hardly depends on the concentration

of Sc beyond the solubility limit, indicating that the contribution of the ScAl_3 phase can be ignored in the resistivity of the Al–Sc alloys. Figure 7 shows that the resistivity increment is linearly proportional to the concentration of Sc. In determining solid solubility by the measurement of electrical resistivity, the contribution of the equilibrium phase can thus be ignored and the resistivity increment must be linearly proportional to the solute concentration. These conditions are satisfied in the present work. Moreover, the thermal treatment of the Al–Sc alloy was carried out in order to attain the equilibrium state at each annealing temperature. Therefore, the solid solubilities determined in the present work may be authentic. This conclusion is also supported by the fact that the solid solubilities of Sc in Al can be represented by one Arrhenius-type equation over the whole temperature range.

There are few reliable results among the previously reported solid solubilities of the 3d transition metals in Al, because the purity of the specimens and the methods of measurement and thermal treatment used were not appropriate. In addition, very few data are available for the solubilities of the 4d and 5d transition metals in Al.

4.2. Excess thermodynamic quantities (Δs and Δh)

Table 4 shows that the values of Δs and Δh for the Al–Sc solid solution are similar to those for the Al–Ti and Al–Mn solid solutions; the very slightly soluble elements have larger values of Δs and Δh . The factors mainly responsible for the heat of mixing are the strain energy W caused by the difference between the atomic radii of the solute and solvent atoms and the valence effect. As the atomic radii of Al and Sc atoms are 1.43 and 1.62 Å, respectively, W may contribute significantly to Δh . It seems that the entropy of vibration and the entropy originating in the temperature dependence of W contribute to Δs .

4.3. Eutectic temperature of the Al-rich side of the Al–Sc phase diagram

Since the solidus temperature shows only a slight concentration dependence and the solidus temperature of the Al–0.198 at.% Sc alloy is 928 K, it may be concluded that the eutectic temperature is also 928 K, in good agreement with the results of Mondolfo [1].

4.4. Residual resistivity of Sc in Al

Our value of the residual resistivity of Sc in Al agrees well with the experimental value of $(3.5 \pm 0.5) \times 10^{-8} \Omega \text{ m (at.\%)}^{-1}$ obtained by Ocko [4] and the theoretical value of $4 \times 10^{-8} \Omega \text{ m (at.\%)}^{-1}$ of Mrosan [5], but disagrees with the experimental value of $5 \times 10^{-8} \Omega \text{ m (at.\%)}^{-1}$ obtained by Fickett [6].

The experimental values of the residual resistivities of 3d transition metals in Al found in the present work and by other workers [4, 6 - 9] are arranged in order of increasing atomic number in Fig. 8, which shows a large broad peak around Cr. This peak is believed to be caused by resonance scattering of the conduction electrons of Al when the position of the virtual

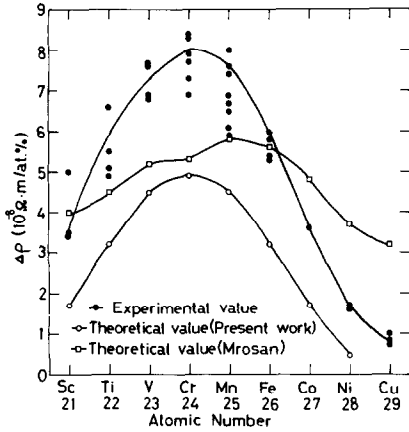


Fig. 8. The residual resistivity of 3d transition metals in Al vs. atomic number.

bound state connected with the impurity is very near to the Fermi energy of Al. Here we will estimate the residual resistivity of 3d transition metals in Al. The residual resistivity [10] is expressed in terms of the phase shifts of the partial waves as follows:

$$\Delta\rho = \frac{4\pi\hbar c}{e^2 K_F Z_A} \sum_{l=0}^{\infty} (l+1) \sin^2(\eta_l - \eta_{l+1}) \quad (2)$$

where \hbar is Planck's constant, c the concentration in atomic per cent, K_F the Fermi wave number for the solvent, Z_A the valence of the solvent and η_l the phase shift corresponding to the l th partial wave evaluated at the Fermi surface. The value of η_1 is required to satisfy the Friedel sum rule

$$Z = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1)\eta_l \quad (3)$$

where Z is the screen charge. In the calculation of $\Delta\rho$ we ignored η_1 except for η_2 because η_2 is dominant owing to the narrow band of d electrons. It is assumed that the screen charges of Sc, Ti, V, Cr, Mn, Fe, Co and Ni are 2, 3, 4, 5, 6, 7, 8 and 9, respectively [9, 11]. Using eqns. (2) and (3), the values of $\Delta\rho$ for 3d transition metals in Al were calculated and are shown in Fig. 8, in comparison with the experimental values and the theoretical value [5] calculated using a muffin-tin impurity model. The theoretical results obtained in the present work give a satisfactory qualitative interpretation of the characteristic maximum.

5. Conclusions

(1) The Al-Sc alloys were prepared from 99.9 wt.% Sc and high purity zone-refined Al. The solubility line of Sc in Al was determined from mea-

measurements of electrical resistivity, paying attention to the conditions of measurement and thermal treatment. The solid solubilities of Sc in Al were determined as follows: 0.186 at.% at 913 K, 0.160 at.% at 893 K, 0.134 at.% at 873 K, 0.117 at.% at 863 K, 0.104 at.% at 853 K, 0.086 at.% at 833 K, 0.068 at.% at 813 K, 0.058 at.% at 793 K, 0.045 at.% at 773 K and 0.033 at.% at 743 K.

(2) The excess entropy of mixing and the heat of mixing for the Al–Sc solid solution were determined from the temperature dependence of the solid solubilities of Sc in Al to be 6.0 R and 59 kJ mol⁻¹, respectively.

(3) On the Al-rich side of the Al–Sc system, Al reacts eutectically with Al and the eutectic temperature is 928 ± 1 K. The maximum solid solubility of Sc in Al was found to be 0.21 at.% at 928 K.

(4) The residual resistivity of Sc in Al per atomic per cent was calculated from the concentration dependence of the resistivity increment at 77 K of Al–Sc alloys to be $(3.4 \pm 0.1) \times 10^{-8} \Omega \text{ m (at.\%)}^{-1}$. The residual resistivities of the 3d transition metals in Al are discussed with the phase shift analysis.

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