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Solid Solubility of Si in Al under High Pressure

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By making use of a 15 mm cubic anvil apparatus, Al-Si alloys of Si-concentration up to 15 at% were studied at a pressure of 54 kbar. The liquidus, solidus and solvus of the Al-rich alloys were determined by means of the 4-probe electric resistance measurement. The solubility limit of Si in Al was extended beyond 15 at% at 54 kbar in comparison with 1.59 at% at 0 kbar. The resistivity of the alloy was increased by a solution of Si with a gradient of $0.5 \mu\Omega\text{cm/at}\%$ up to 15 at%Si. The alloy quenched under high pressure was examined by X-ray diffractometry showing that Si was completely solid-dissolved in Al. The quenched alloy was much more hardened than the ordinary two-phase alloy at 0 kbar.

§1. Introduction

Under ordinary pressure the Al-Si alloy, known as an important casting material, is a simple substitutional alloy forming no inter-metallic compound, and has a eutectic at 11.3 at%Si and 577°C . Practically the solubility limit of Si in Al is 1.59 at% at the eutectic temperature, and the solubility of Al in Si is almost null.

While no work at high pressure has been reported, a lot of studies on the physical and metallurgical properties of this alloy have been made at ordinary pressure such as those of the precipitation of Si from Al-rich Al-Si alloys through the electron microscopy and the electric resistance measurement by Rosenbaum and Turnbull,^{1,2)} Ozawa and Kimura³⁾ and van Gorp,⁴⁾ and that of the solubility limit of Si in Al through the electric resistance method by Kovács-Csetényi, Vassel and Kovács.⁵⁾

So far the present authors studied a phase diagram of the Al-rich Al-Si system at 28 kbar by means of a girdle-type high pressure apparatus and the electric resistance method, and it was made clear that the melting point of Al increased to 840°C at 28 kbar from 660°C at 0 kbar and the eutectic moved to 660°C , 17.5 at% Si at 28 kbar from 577°C , 11.3 at% Si at 0 kbar.⁶⁾ The solubility limit of Si in Al was determined by the micrographical examination of the quenched samples. Then it was found that the solid solubility of Si in Al was significantly extended to 10 at% Si at 28 kbar in contrast to 1.59 at% Si at 0 kbar.

The present paper is concerned with the extended study of the same alloy to 54 kbar in which to determine in detail the liquidus, solidus and solvus of Si in the Al-rich alloys a cubic anvil press and a 4-probe method have been used as the pressure apparatus and the precise electric resistance measurement, respectively. Also to obtain the supersaturated alloy, the Al-rich Al-Si alloys were quenched under high pressure. And then the X-ray diffraction, the micrographical observation and the hardness test were made on the quenched alloys.

§2. Experimental

2.1 High pressure apparatus

In Fig. 1 is shown the high pressure apparatus which is composed of a 15 mm cubic anvil press of WC and the steel guide blocks. The top and bottom anvils are fixed to the blocks [5] and [6], respectively. Each of [5] and [6] has the 45° -inclined guide surfaces. The side anvil [1], dividing the vertical uniaxial load into components by the wedge action due to the inclined surfaces of the block, is advanced by the same amount synchronizing with the motions of the top and bottom anvils to the center of the pressurized cubic region. Each of the sliding surfaces between the side anvils and the guide blocks is well lubricated by both of MoS_2 and Teflon sheet. The motions of the top and bottom guide blocks are precisely aligned by means of the four robust guide pins each 65 mm in diameter. This high pressure apparatus is driven by a 1200 ton hydraulic press equipped with a constant loading controller.

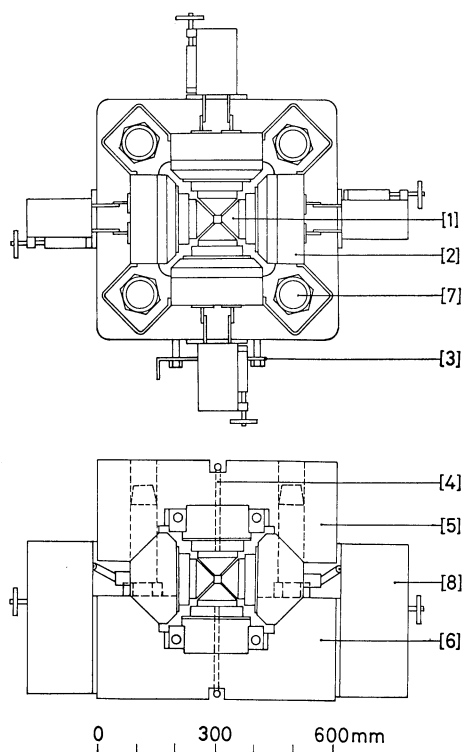


Fig. 1. Cubic anvil apparatus. [1] Anvil. [2] Anvil support. [3] Current terminal for heating, [4] Cooling water duct, [5] Top guide block, [6] Bottom guide block, [7] Guide pin, [8] Anvil puller.

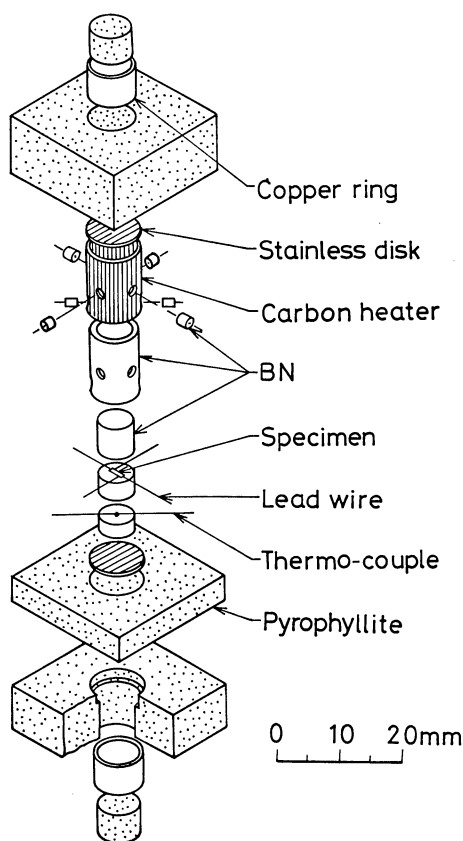


Fig. 2. Pressure cell assembly.

The current for heating sample is supplied from a 3 kW source whose power is controlled by means of the Hall element and the thyristor. This current flows from the heating current terminals [3], which contact to the top and bottom anvils, respectively. And then it flows in the cylindrical carbon heater within the pressure cell. To prevent the overheating of the anvils, cooling water circulates in the top and bottom anvil blocks through the ducts [4].

2.2 Pressure cell and samples

In Fig. 2 is shown the assembly of the pressure cell. The cell whose edge was 20 mm long each was formed from the pyrophyllite baked at 500°C for 1 hr. The electric current for heating the sample flows through copper rings to the carbon heater. Inside the cylindrical carbon heater a sleeve and disks of boron nitride (BN), the alloy sample and a Pt-Pt13%Rh thermocouple of 0.3 mm o.d. were inserted. A pure aluminum wire 0.3 mm o.d. was used as the lead-wire for measuring the electrical resis-

tance, and each of the current and potential difference lead-wires was connected to one of the four anvils. The BN and the carbon was preheated in vacuum at 1000°C for 1 hr for evacuating gases in advance. Both of the aluminum lead-wire and the thermocouple were insulated from the carbon heater by means of the thin BN tubes 2 mm o.d.. The thermocouple was taken out through the gap between the anvils.

Sample alloys were prepared by following ways. The mixture of zone-refined 99.999% Al and 99.999% Si in the desired composition was melted in the alumina crucible. In this process the mixture of NaF and NaCl was floated on the molten alloys as flux to prevent the oxidation of alloy. And then molten alloy was sucked in 3 mm i.d. Pyrex tube, and was solidified *in situ*. Compositions of the sample alloys thus obtained were determined to be Al-3.7, 7.0, 11.4 and 14.9 at%Si by the wet analysis. To make the samples for measuring electric resistance, these cast alloys and pure Al

were rolled into thin pieces 0.01 mm thick, 6 mm long and 0.5 mm wide, and then annealed in vacuum at 400°C for 3 hr to release any residual stress or strain. And 1.5 mm d. wire-drawn sample alloys were also used as the samples for X-ray measurement, microscopic observation and hardness testing. The grain size of the sample alloy and pure Al was about 0.02 mm.

2.3 Experimental procedure

Throughout the present experiment the press load was increased at a fixed rate 8 ton/min until the fixed load value 800 ton was attained. The press load of 800 ton was calibrated to 54 kbar at the sample site by using the fixed points such as Bi_{I-II}(25.4 kbar), Tl_{II-III}(36.7 kbar) and Ba_{I-II}(55 kbar).

The sample was heated at a rate of 2°C/min. In addition to record the electric resistance of the sample continuously, precise resistance measurements were performed by a digital micro-voltmeter every 50°C steps keeping constant temperature for 30 min to 2 hr. This time duration was required to solution of Si in Al. In the present 4-probe method, by flowing a calibrated constant current 100.000 mA the potential difference between the both ends of the sample could be read with five digits. Also to avoid the errors such as due to the thermal emf and the contact potential difference, the resistance measurement was made several times by alternating the current direction.

To confirm the solution of Si in Al the quenching of the sample from high temperature and high pressure to the ordinary temperature and pressure was performed. Sample alloys Al-7.0 at%Si were solution-treated at 54 kbar by three ways such as 420°C for 2 hr (denoting 2HR420), 420°C for 10 hr (10HR420) and 600°C for 2 hr (2HR600). These samples were quenched to room temperature by shutting off the heating current with a cooling rate of about 140°C/sec. The quenched samples were examined by the X-ray diffraction measurement, the microscopic observation and the Vickers-hardness testing.

§3. Results and Discussions

3.1 Temperature dependence of electric resistance of Al-rich Al-Si alloy

In Fig. 3 is shown the electric resistance vs.

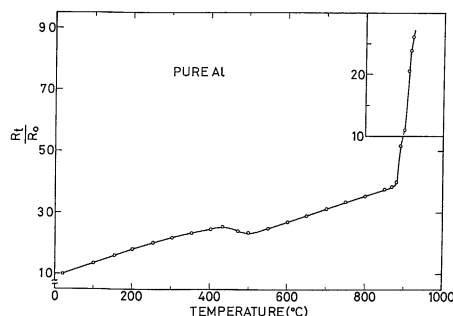


Fig. 3. Electric resistance vs. temperature relationship of pure Al at 54 kbar.

temperature relationship obtained by the pure aluminum. R_t/R_0 in the ordinate means the ratio of the resistance value at $T^\circ\text{C}$ to the value at room temperature. The curve was taken during the first time heating after the pressurization to 54 kbar.

In the pure aluminum the resistance increases linearly with temperature up to 200°C, and after that its temperature derivative decreases slightly and the resistance maximum is attained at about 420°C, but the resistance increases again linearly from 500°C to the melting point. To examine the apparent resistance anomaly in the range from 200°C to 500°C, measurements of electric resistance were continued between the room temperature and 600°C repeating alternate heating and cooling. As shown in Fig. 4, a linear relationship was obtained at the second time heating. Though the causes of the resistance anomaly shown in the first run can not be elucidated in the present experiments, it should be considered that the sample is much or less affected by the complex shear stresses and strains and some lattice defects due to the

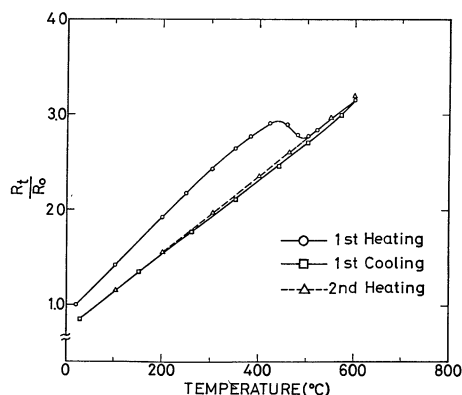


Fig. 4. Electric resistance change by alternate heating and cooling cycles on pure Al at 54 kbar.

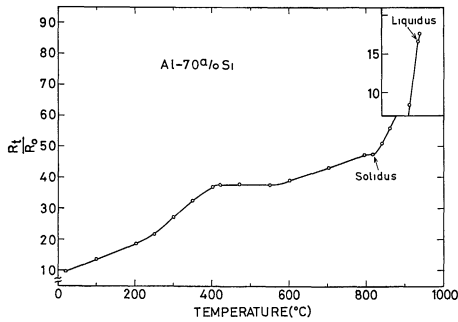


Fig. 5. Electric resistance vs. temperature relationship of Al-7.0 at%Si alloy at 54 kbar.

deformation during the pressurization. This anomaly, therefore, should be taken place by the recovery of their shear stresses or defects.

The electric resistance vs. temperature relationship of Al-7.0 at%Si alloy was shown in Fig. 5. In this case the temperature derivative of the resistance was increased from 200°C by the solution of Si in Al. The resistance increment due to the solution of Si, however, was superposed on the recovery of the resistance over the range from 200°C to 500°C. Thus it was hard from Fig. 5 to identify the solid-solubility of Si. Moreover in this experiment Si could not be precipitated from the solution even by annealing at 200°C for 10 hr under 54 kbar. It was, therefore, impossible to detect the resistance increment due to the solution of Si by the second time heating process as shown in Fig. 4.

Both of the liquidus and the solidus, on the other hand, could be readily assigned from Fig. 5 to 930°C and 820°C, respectively.

3.2 Solubility limit of Si in Al

Just as mentioned above it is very hard to identify directly the solubility limit of Si in Al from the electric resistance vs. temperature measurements. Here by taking the difference in the shape among the sample into account, the resistance vs. temperature relationship has been first transferred to the resistivity vs. temperature relationship. Then from the resistivity difference between the pure Al and the alloy at an identical temperature the resistivity increment $\Delta\rho_{Si}$ accompanied with solution of Si in Al has been obtained.

The electric resistance R_{Al} of the pure Al and R_{Al-Si} of an alloy would be expressed as follows;

$$R_{Al} = k(1 + \alpha T)\rho_{Al}, \quad (1)$$

$$R_{Al-Si} = k'(1 + \alpha T)\rho_{Al} + k'\Delta\rho_{Si}, \quad (2)$$

where k and k' are coefficients depending on the sample shape, T the temperature and ρ_{Al} and α the resistivity of the pure Al annealed under high pressure and its temperature coefficient, respectively. From eqs. (1) and (2), the resistivity increment accompanied with solution of Si in Al is expressed as

$$\Delta\rho_{Si} = R_{Al-Si}/k' - R_{Al}/k. \quad (3)$$

In the present study k and α have been determined from eq. (1) by the present measurements of R_{Al} at 20°C under 54 kbar, along with the value of ρ_{Al} 2.25 $\mu\Omega\text{cm}$ at 20°C under 54 kbar. This value of ρ_{Al} at 54 kbar is reduced from resistivity 2.75 $\mu\Omega\text{cm}$ at 0 kbar using Bridgman's measurement⁷⁾ of electric resistance vs. pressure relationship. Also from eq. (2) k' and $\Delta\rho_{Si}^{\text{max}}$, the resistivity increment at the completely dissolved state of Si into Al, have been determined using the ρ_{Al} and α just obtained. Meanwhile with the values of R_{Al} and R_{Al-Si} measured during the first time heating along with the pertaining values of k and k' , eq. (3) gives the numerical values of the resistivity increment $\Delta\rho_{Si}$ due to the solution of Si in Al.

Figure 6 shows the $\Delta\rho_{Si}$ vs. temperature rela-

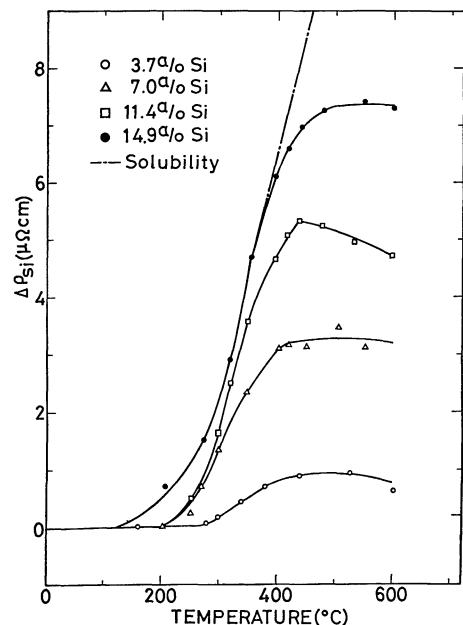


Fig. 6. Resistivity increment, $\Delta\rho_{Si}$, due to solution of Si in Al as a function of the temperature.

tionship thus obtained. The figure reveals that the solution of Si in Al begins at about 200°C and then the $\Delta\rho_{\text{Si}}$ value is increased along the solubility limit up to its saturated value $\Delta\rho_{\text{Si}}^{\text{max}}$. The fact that there is a slight inconsistency in the solubility limits of the samples tested should be attributed to that the thermal equilibrium of the sample has not been attained completely due to the extremely low mobility of Si in the alloy under high pressure. Since the most reliable measurement of $\Delta\rho_{\text{Si}}$ in Fig. 6, therefore, would be on the sample Al-14.9 at%Si, the solvus line was determined from the measurements on Al-14.9 at%Si.

In Fig. 7 is shown the $\Delta\rho_{\text{Si}}^{\text{max}}$ vs. Si-content relationship. The scattering of these measured points is not so large that the before-mentioned procedure for determining the solubility limit of Si would be reasonable. From the slope of this relationship 0.5 $\mu\Omega\text{cm/at}\%$ Si is obtained as the resistivity increment due to the solution of Si in Al 54 kbar. In comparison with the value 0.7 $\mu\Omega\text{cm/at}\%$ Si by Kovács-Csetényi *et al.*⁵⁾ at 0 kbar, the resistivity increment should be decreased at high pressure. Along with the fact that the resistivity of metals is decreased with pressure in general, the present result should be reasonable.

In Table I are shown the liquidus, the solidus and the solvus temperatures obtained by the

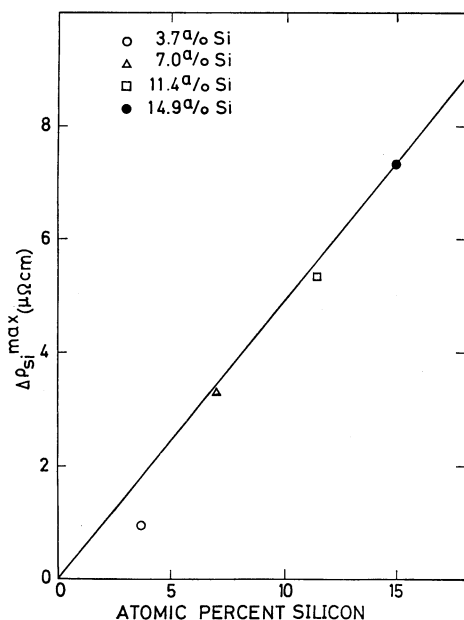


Fig. 7. Maximum of $\Delta\rho_{\text{Si}}$ in Fig. 6, $\Delta\rho_{\text{Si}}^{\text{max}}$, as a function of Si-concentration.

Table I. Liquidus, solidus and solvus temperatures under 54 kbar.

at%Si	Liquidus temperature (°C)	Solidus temperature (°C)	Solvus temperature (°C)
0	970		
3.7	940	910	280
7.0	930	820	320
11.4	900	790	380
14.9	890	700	420

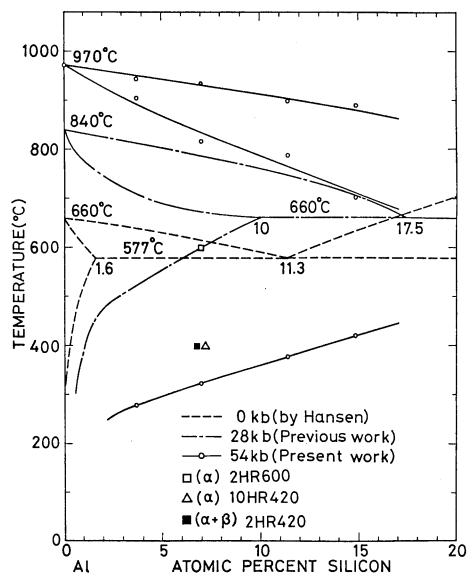


Fig. 8. Al-side phase diagram of Al-Si alloy at high pressure.

present study. These temperatures are measured by the Pt-Pt13%Rh thermocouple under high pressure. Though emf of thermocouple is affected by pressure in general, in the present experiment the pressure effect of emf is not taken into account, since it is too difficult to correct exactly. It is considered that these temperatures give the lower values by about 5% at 54 kbar.⁸⁾ Also in Fig. 8 the phase diagram of Al-Si system obtained in the present study is shown in comparison with those at 0 kbar⁹⁾ and 28 kbar by the present authors.⁶⁾ The melting point of the pure Al increase to 970°C at 54 kbar from 660°C at 0 kbar giving the mean pressure derivative 5.7°C/kbar. Since within 28 kbar a value 6.4°C/kbar had been obtained previously, the pressure dependence of the melting point would be diminished with higher pressure. The solubility limit of Si was markedly extended to about 15 at% at 54 kbar from 1.6

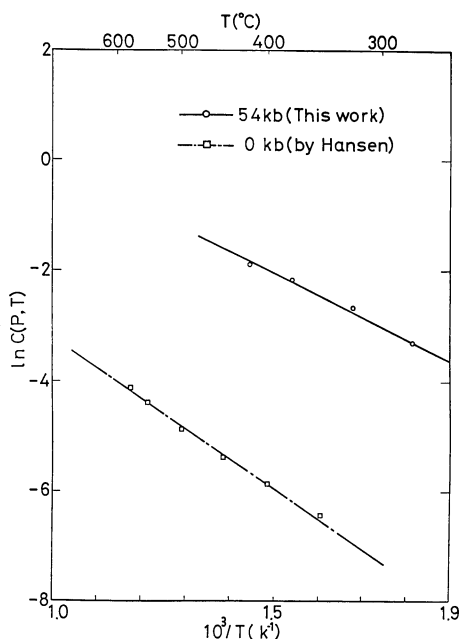


Fig. 9. Solute Si-concentration in Al as a function of the reciprocal temperature.

at % at 0 kbar.

In Fig. 9 are shown solute Si concentration vs. reciprocal temperature relationships obtained from the solvus line in Fig. 8. According to Fig. 9 the logarithm of the solute Si concentration is a linear function of the reciprocal temperature. This means that the solute concentration C can be written as

$$C = C_0 \exp(-\Delta H/kT), \quad (4)$$

where ΔH is the activation enthalpy for solution. From the data of Fig. 2 we find 0.32 eV at 54 kbar. Compared with 0.46 eV at 0 kbar, it is found that the activation enthalpy for solution of Si in Al is decreased with pressure.

The activation enthalpy ΔH should be written as $\Delta H = P\Delta V + \Delta E$, where P is pressure and ΔV and ΔE are the activation volume and energy for solution, respectively. Since the lattice of Al is contracted by the solution of Si,¹⁰⁾ ΔV should be negative. Then the present result for the pressure dependency of the activation enthalpy seems to be reasonable.

3.3 Quenching of samples

Based on the phase diagram shown in Fig. 8, to investigate the solid-solution of Al(Si), quenching from high temperature and high pressure was performed on the Al-7.0 at %Si

alloy on which the existence of the precipitated Si has been examined by the X-ray diffraction. The results were such that while the faint diffraction lines of Si remained in 2HR420 showing an incomplete solution-treatment, they disappeared completely for the specimens 10HR420 and 2HR600. This shows that a longer time should be needed to make solution of Si in Al under high pressure, but the solid-solution of Al(Si) could be quenched to the ordinary temperature and pressure. Since the precipitated Si in the quenched alloy sample except 2HR420 was not also detected by the micrographical examination, the above results were supported.

Vickers-hardness testing was also performed on the quenched samples, giving $H_v = 61, 82$ and 83 for samples 2HR420, 10HR420 and 2HR600, respectively. Comparing to the original hardness $H_v = 41$ of the annealed alloy, the hardness of the solution-treated alloy was almost doubled.

§4. Concluding Remarks

In making use of a 15 mm cubic anvil apparatus, the phase diagram of Al-rich Al-Si alloy was determined under 54 kbar. Samples employed were a pure Al and four Al-Si alloys containing Si ranging from 3.7 to 14.9 at %. The liquidus, the solidus and the solvus of Si in these alloys were determined by means of the 4-probe measurement of the electric resistance.

Results obtained follow;

(1) In the pure Al the melting point increases to 970°C at 54 kbar from 660°C at 0 kbar with the mean pressure derivative of 5.7 °C/kbar.

(2) To give the resistivity increment due to the solution of Si in Al, the resistivity of the pure Al was subtracted from the alloy resistivity. At 54 kbar this resistivity increment was 0.5 $\mu\Omega\text{cm/at}\%\text{Si}$. By this method, it was shown that the solid solubility of Si in Al was extended to 15 at % 54 kbar from 1.6 at % at 0 kbar. The activation enthalpy for solution of Si in Al, which was obtained from the solvus line, was 0.32 eV under 54 kbar, and it was decreased with pressure.

(3) Completely solution-treated Al-7.0 at %Si samples have been quenched from high temperature and high pressure state. X-ray

diffraction and the microscopic examination made on these samples show that Si has been completely dissolved into the Al matrix. Vickers-hardness testing was also made on these alloys showing that the hardness of the quenched alloy has been doubled compared to that of the annealed alloy.

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