P-V-T Relation in Aluminum as Pressure and Temperature Scale under Very High Pressure*

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A pressure-volume-temperature relation in aluminum was calculated by pseudopotential method and Mie-Grüneisen relation. The thermal dilatation data of aluminum showed good agreement with this calculated value. The calculated results under very high pressure and high temperature environment were compared with NaCl scale by a newly designed X-ray diffraction system with a LiF monochrometer at the receiving slit. Both scales just fitted within an error range. It can be concluded that the proposed aluminum scale is acceptable under very high pressure.

Key Words: Very High Pressure Scale, Measurement, Aluminum, Equation of State, X-Ray Diffraction, Pseudopotential

1. Introduction

The science and technology for very high pressure and high temperature are essential to development of abrasive materials, cutters or new ceramic materials. The determinations of generated pressure, temperature and stress state in the cell are inevitable problems in the developement of the very high pressure technology.

There are several types of pressure generating devices (i.e., opposed anvils, girdle, belt, tetrahedral and cubic types), however, it is unsuitable to determine the generated pressure as load divided by area. Moreover, the difficulties of pressure measurement will increase in internal heating systems, because the mechanical properties and the thermal dilatation will vary under elevated temperature. Thus, it is not easy to determine the pressure and the temperature simultaneously under very high pressure and high temperature.

The purpose of this study is to propose a new standard material for the determination of the pressure and/or temperature by p-v-T (pressure, atomic volume and temperature) relation. Decker[1] earlier proposed the p-v-T relation of NaCl for this purpose (hereafter called the NaCl scale). However, NaCl has a phase transition from B1 to B2 at about 30 GPa and room temperature, so it is difficult to apply the scale beyond this pressure range. Several kinds of such pressure scales have been proposed[2].

We have calculated the internal energies for some elements using a pseudopotential method which is effective for simple metals having nearly spherical Fermi surfaces. From the volume derivatives for these energies, the p-v relations for these metals were calculated and the values obtained show good agreement with the experimental ones[3].

A calculated p-v-T relation in Al is presented here by this method and the temperature effect is corrected by the Mie-Grüneisen relation, which has a different theoretical basis from a typical ionic crystal such as NaCl. The applicability of these p-v-T relations for Al and NaCl is confirmed by a newly improved high-temperature, high-pressure X-ray diffractometry.

2. Theoretical Background and Calculation

2.1 Internal energy

The authors have proposed new model potentials obtained by improvement of that of Heine-Abarenkov-Animal, and from these potentials, they determined internal energies of metals under very high pressure environment (i.e., under large volume change). By this method, the p-v relations in several metals such as sodium, potassium, rubidium, cesium, calcium, aluminum, silicon and germanium were calculated[3]. The results agreed well with the experimental values except in the case of calcium.

The model potential $W(r)$ is

$$W(r) = -A \quad (r \leq R_M)$$
$$W(r) = -Ze^2/(4\pi\epsilon_0 r) \quad (r > R_M) \quad \cdots(1)$$

where A is the depth of potential well, R_M is the radius of the model, Z is the atomic valency, e is the electron charge and r is the radius. The total energy of metal at 0 K, U_t, is written by second perturbation as the sum of the following four

terms; the energy of conduction electron gas, U_{eg}, the electro-static energy of ions immersed in conduction electron gas, U_{es}, the average value of the electron-ion interaction energy, U_0, and the band structure energy, U_{bs}.

$$U_t = U_{eg} + U_{es} + U_0 + U_{bs} \quad \cdots\cdots\cdots\cdots\cdots (2)$$

The band structure energy, U_{bs}, is expressed[4] as

$$U_{bs} = \sum_q {}'|S(q)|^2 [W(q)]^2 \chi(q)\varepsilon(q) \quad \cdots\cdots (3)$$

where $S(q)$ is the structure factor of metallic crystal, $W(q)$ is the Fourier transformation of model potential, $W(r)$, in Eq.(1), $\chi(q)$ is the perturbation characteristic, $\varepsilon(q)$ is the dielectric function, and q is the reciprocal lattice vector. $W(q)$ was taken as zero beyond the point of $q=8k_f$ in the present calculation, but in the former one, up to $q=4k_f$[3], where k_f is the Fermi wave number. As a consequence, 28 sets of reciprocal lattice point were considered. Also, the atomic volume of Al at 0 K was revised to a newly accepted one, 1.638×10^{-29} m^3. Considering this revision, the potential parameter is redetermined by the same procedure[3]. The parameter obtained are as follows; $R_M = 7.1599 \times 10^{-11}$ m, $A = 3.9005 \times 10^{-18}$ J.

2.2 P-v-T relation in Al

Since the pressure vs. volume relations obtained in section 2.1 are at 0 K, the relations are extended to a elevated temperature range by using the Mie-Grüneisen equation of state. According to Girifalco[5], the pressure p_T at temperature T is expressed by the following equation;

$$P_T = P_0 + 3k\Theta\gamma D_\varepsilon(\Theta/T) \quad \cdots\cdots\cdots\cdots\cdots (4)$$

where γ is the Grüneisen constant, Θ is the Debye temperature, p_0 is a pressure at 0 K, and k is the Boltzmann constant. $D_E(\Theta/T)$ is the Debye function which is defined as

$$D_\varepsilon(x_D) = \frac{3}{x_D^3}\int_0^{x_D}\frac{x^3 dx}{e^x - 1}, \quad x_D \equiv \frac{h\nu_D}{kT}$$

where h is Planck's constant and ν_0 is the Debye frequency. We employed an experimental value 2.34 as γ_0[5] which is a value at room temperature, and 410K as the Debye temperature Θ which is deduced from an experimental value of elastic constant in Al[6]. For a volume dependency of γ and Θ, we employed the following expression as in the well-known p-v-T relation of NaCl by Decker[1].

$$\gamma = \gamma_0(V/V_0)^a \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (5)$$

$$\Theta = \Theta_0 \exp\{(\gamma_0 - \gamma)/a\} \quad \cdots\cdots\cdots\cdots\cdots (6)$$

where a is a constant close to unity. We employed a=1 for the above Eqs.(5) and(6).

2.3 Calculation

The p-v-T relation in Al up to 100 GPa, and 1000 °C calculated by the procedure in the section 2.3 is shown in Table 1. The atomic volume decreases by 20% at 27 GPa and room temperature. However, compressibility will decrease under higher pressures, and a volume decrease will be only 38 % even at 100 GPa. Figure 1 shows a comparison of calculated and experimental data of temperature vs. volume at atmospheric pressure. They both agree well and from this result the employed data are found to be acceptable.

Table 1 Calculated values of relative volume (v/v₀), temperature (°C) and pressure (GPa) in aluminum

V/V₀	0K	25°C	200°C	400°C	600°C	800°C	1000°C
1.06	-4.84	-3.75	-2.77	-1.63	-0.47	0.69	1.85
1.04	-3.69	-2.63	-1.66	-0.51	0.64	1.80	2.96
1.02	-2.42	-1.39	-0.42	0.72	1.88	3.04	4.20
1.00	-1.01	0.00	0.96	2.10	3.26	4.41	5.58
0.98	0.57	1.54	2.50	3.64	4.79	5.95	7.11
0.96	2.31	3.27	4.22	5.35	6.50	7.66	8.82
0.94	4.26	5.18	6.13	7.26	8.41	9.56	10.72
0.92	6.43	7.32	8.26	9.39	10.53	11.69	12.85
0.90	8.85	9.71	10.64	11.77	12.91	14.06	15.22
0.88	11.55	12.38	13.31	14.42	15.56	16.71	17.87
0.86	14.57	15.37	16.28	17.39	18.53	19.68	20.84
0.84	17.94	18.71	19.61	20.72	21.86	23.00	24.16
0.82	21.72	22.46	23.35	24.45	25.58	26.73	27.88
0.80	25.96	26.66	27.55	28.64	29.77	30.91	32.06
0.78	30.72	31.39	32.27	33.35	34.48	35.62	36.77
0.76	36.08	36.72	37.58	38.66	39.78	40.92	42.06
0.74	42.12	42.73	43.58	44.65	45.76	46.90	48.04
0.72	48.95	49.53	50.36	51.42	52.53	53.66	54.81
0.70	56.68	57.23	58.05	59.10	60.20	61.33	62.47
0.68	65.47	65.98	66.78	67.82	68.92	70.04	71.18
0.66	75.46	75.95	76.73	77.76	78.85	79.97	81.10
0.64	86.88	87.33	88.09	89.11	90.20	91.31	92.44
0.62	99.95	100.38	101.12	102.12	103.20	104.31	105.44
0.60	114.98	115.37	116.09	117.09	118.15	119.26	120.38

3. Experimental

For the purpose of checking the reliability of the calculated values, X-ray diffractometry was used to compare the observed lattice constants in NaCl and in Al specimens which were adjacent to each other under high-pressure high-temperature environment.

3.1 Experimental procedures

For the generation of a high-pressure, high-temperature environment, a DIA6 cubic anvil high-pressure high-temperature device with rotating-target type X-ray generator (60 KV, 200 mA) which has already been described by Senoo[9] is employed. Usually, X-ray diffractometry under elevated temperature and high pressure has the following difficulty compared with that at room temperature.

(1) There must be a geometrical arrangement of the internal heater without any interference in the X-ray path.

(2) Pressure transmitting media should have not only X-ray transparency but also a good thermal insulator under high pressure high temperature.

(3) A preferred orientation of the sample caused by recrystallization and crystal growth under high temperature must be prevented, as well as the error caused by a shift of the effective diffraction center induced by this preferred orientation. For these problems, a newly designed pressure cell arrangement and the X-ray diffraction method are employed.

3.2 Pressure cell and samples

Two types of pressure cells are employed. Cell A is composed of 33% amorphous boron powder and 67% polyester resin. After hardening of these mixtures, the cell is baked at 250 °C, 5 h in a vacuum. Cell B is composed of 50% silicone which can withstand high temperature and 50%
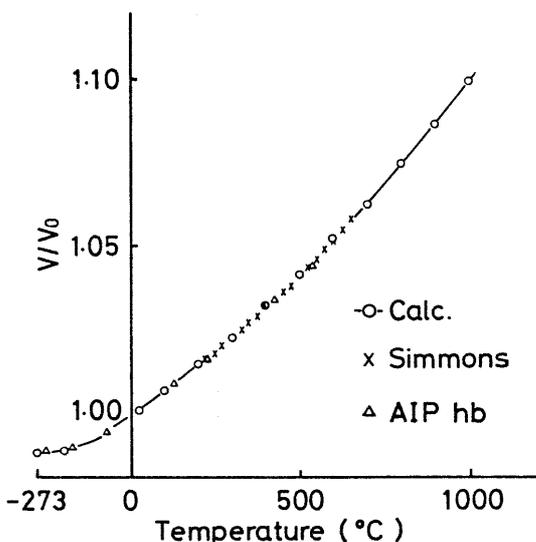
amorphous boron powder, and baked at 300 °C, 2 h in a vacuum. Figure 2 shows the geometric arrangement of the cell employed. In this cell, the current lead is 0.06 mm-thick with a 0.6 mm-wide silver ribbon; the heater is 0.04 mm-thick with a 2 mm-wide Kanthal ribbon, and the thermocouple is 0.3 mm in diameter (Pt/Pt13%Rh). Two thermocouples are inserted in the cell, with one junction between Al and NaCl (center of the cell), and the other between NaCl and the insulation mica (near the heater ribbon). To prevent crystal growth and the preferred orientation in the specimen of pure Al (99.999%) and in NaCl (99.99%), the following procedure is used. A pure aluminum ingot is filed and sieved by #1200 mesh, and mixed with a heat-resisting binder (Sauereisen #14). This mixture is press-formed to a pellet shape sample, and baked at 300°C, 3 h in a vacuum. The NaCl sample is press-formed to the fixed dimensions at about 0.5 GPa from mortared NaCl fine powder.

3.3 Receiving monochrometer

Figure 3 shows the X-ray optical system employed. The monochrometer is 10x15 mm square, with a 5 mm-thickness flat LiF mono-crystal and fitted on the 2θ goniometer arm in front of the NaI X-ray detector. By adjusting the $2\theta_2$, only an X-ray with a specified wave length which
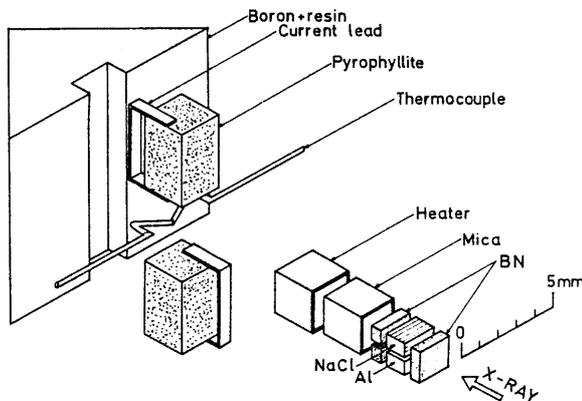

Fig.2 Geometric arrangement of the pressure cell for high-temperature high-pressure X-ray diffractometry

Fig.1 Comparison between calculated and observed values of the thermal dilatation in Al
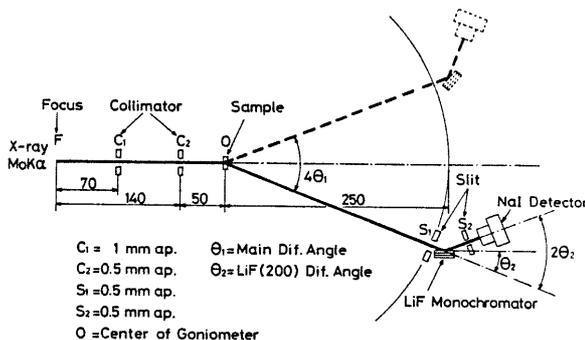

Fig.3 X-ray optical system

is diffracted from the center of the goniometer satisfies the diffraction condition. When the specimen shifts induced by the heating or the pressing, the error can be corrected to obtain the maximum reflection intensities for each diffraction line. Also, at high temperature especially near the melting point, the effective diffraction center usually shifts by the grain growth and/or the recrystallization of the specimen. The error due to this effect is often not small at high temperature in a high-pressure experiment. The above-mentioned process is effective for this error correction. The total standard error of the measurement of lattice constant in this X-ray diffractometry is ±0.02%, and this is almost the same as that of room temperature high-pressure diffractometry in the former report[9].
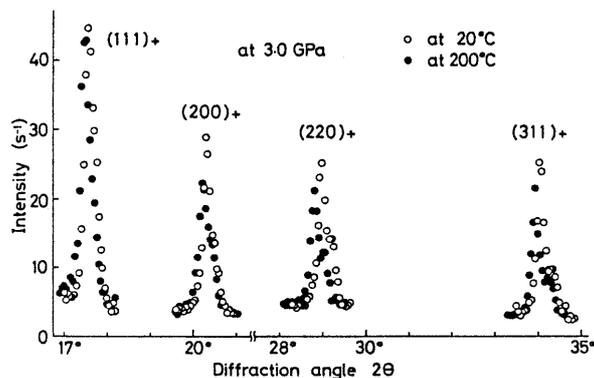
Figure 4 shows the diffraction patterns for various specimen positions where the shift values show the off-center of the specimen along the incident X-ray. The pattern in this figure shows the diffraction intensities of (111) plane in Al under 3 GPa at 200 °C. It is obvious in Fig. 3 that the reflections of the monochrometer crystal and the sample are antiparallel on the upper side (shown by dotted line in Fig. 3) and marked + in Figs. 4 and 5, and parallel on the lower side (shown by solid line). Usually, the antiparallel configuration has a better resolution.

In this system, the X-ray intensity in the detector decreases as compared with the usual system, because the efficiency of the monochrometer is less than unity. However, the fluorescent X-ray or white X-ray from the sample and/or pressure cell can be separated from diffracted lines, and the total background noise decreases; then the S/N ratio is improved. Even in a high-temperature high-pressure environment, sharp diffraction lines are obtained as shown in Fig. 5. This figure shows the line profiles in Al at 20 °C and at 200 °C. Each point is obtained at 20 s and at every 5/100° scanning step.

4. Results and Discussion

Firstly, a comparison was made between the calculated p-v relation on Al and the observed bulk compression and shock wave data. The reliability of the calculated p-v relation was checked in Al. Secondly, the compatibility of Al scale and NaCl scale was confirmed by high-temperature high-pressure diffractometry.

Figure 6 shows the difference in experimental values between the pressures in Al scale and in NaCl scale; it also shows the bulk compression data in Al by Vaidya-Kennedy's piston cylinder experiment[10], Bridgman's compression data[11], and the p-v relation in Al by shock wave data[11]. As shown in Fig.6, the difference between pressures in Al scale and in NaCl scale is within ±0.2 GPa. This means that two pressure scales have no difference within the error range. In this figure, Bridgman's data have been revised by recent pressure standard. Vaidya and Kennedy's compression
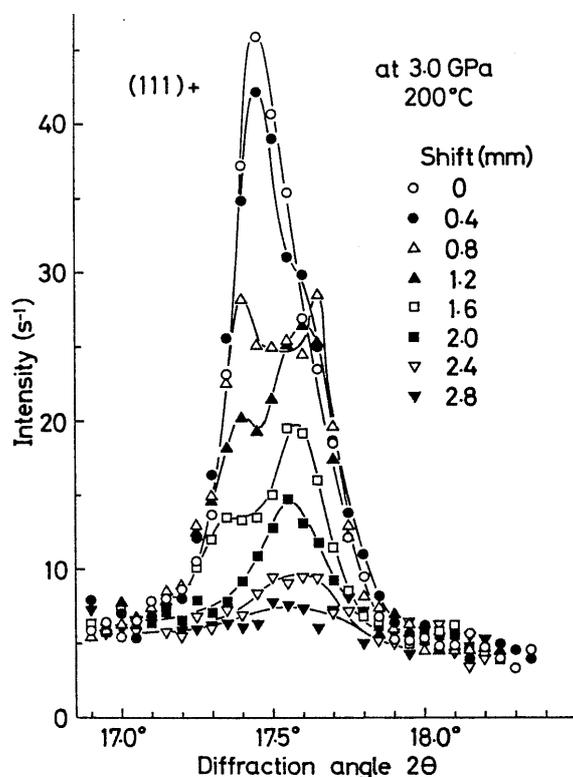

Fig.4　Change of diffraction line profiles in Al induced by the sample position shift

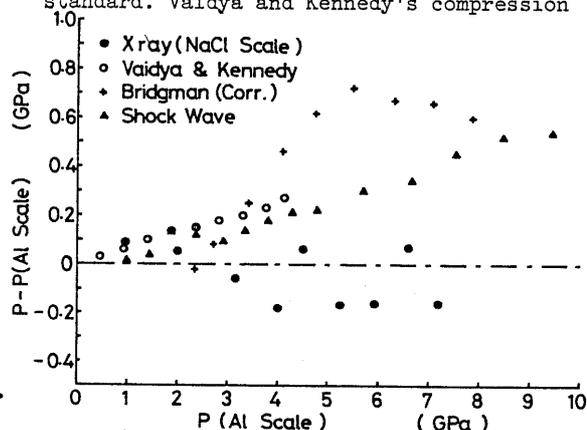Fig.5　Diffraction patterns in Al at high and room temperatures

Fig.6　Comparison between Al scale and other compression data including NaCl scale at room temperature

data and shock wave data in Al are about 5% higher than those of the present scale. However, at higher pressure this discrepancy becomes smaller in the case of shock wave data, e.g., a difference of +5% at 50 GPa and 4% at 80 GPa.

The difference between Al and NaCl scales at 7 GPa at elevated temperature is shown in Fig. 7. The ordinate indicates the difference between the pressure obtained by X-ray diffraction data in Al and the data in Table 1, and the pressure by NaCl diffraction data at each temperature. The difference of both scales is within 0.2 GPa in all temperature ranges. From the above-described findings, it is concluded that both scales agree well within the experimental error.

Figure 8 shows the pressure shift in the cell due to a change of the temperature under constant loading. Pressure hysteresis in the cell A and B are indicated by blank and solid circles, respectively. There are small differences in the hysteresis caused by the difference in the cell thermal characteristics. The characteris-
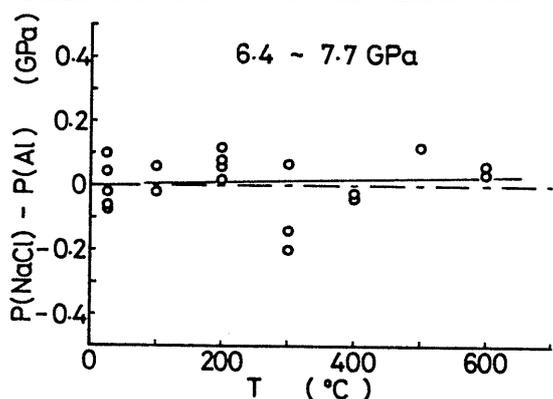

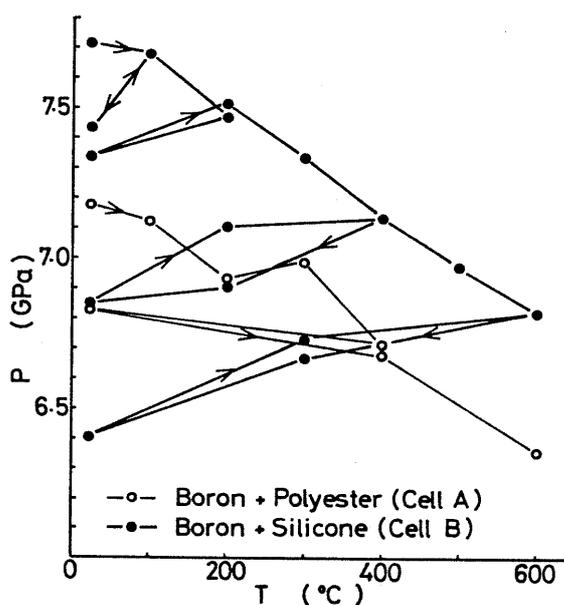Fig.7 Comparison between Al and NaCl scale at elevated temperature

Fig.8 Pressure shift in the cell by temperature change under constant loading

tics of the hysteresis are summarized as follows.
(1) The first and second heating processes are different.
(2) The first cooling and the second heating process are almost the same.

In the first heating in the cell A (polyester), the pressure decreases at a rate of -0.13 GPa/100 °C, and in the first cooling and the second heating, the pressure seems to be constant within an experimental error. On the other hand, in the first heating in the cell B(silicone), the pressure also decreases at -0.15 GPa/100 °C. However, in the first cooling and the second heating, the pressure increases at a rate of 0.07 GPa/100 °C. The pressures decrease in the first cooling for both cells. This fact implies that the effect of the thermal dilatation in the pressure media is less than that of the decrease in the flow stress and the stress relaxation of the pressure media at an elevated temperature. At the second heating, where the stress relaxation is already completed, the phenomenon (2) seems to appear.

NaCl and Al have different cohesive mechanisms, and both scales agree well within an experimental error. This means that both scales are consistent and have high reliability as the pressure scale.

5. Concluding Remarks

The p-v-T relationship up to 100 GPa and 1000 °C in Al for a new pressure scale was calculated by the pseudopotential methods using a model potential proposed by the authors in the former report and Mie-Grüneisen relation. The Al scale was compared with the NaCl scale experimentally by high-temperature high-pressure X-ray diffraction. The results obtained are summarized as follows.
(1) This p-v-T relation in Al is appropriate for the new pressure scale, and it can be applicable beyond 30 GPa, because Al has no pressure-induced phase transition. And also Al has a simple crystal structure and X-ray diffraction patterns are easily obtained.
(2) The lattice constants in Al and NaCl up to 7 GPa and 600 °C were measured, and the difference in both pressures obtained by the lattice constants was negligible within an experimental error. Al is, therefore, an appropriate standard material for the determination of pressure and temperature under very high pressure environment.
(3) The new X-ray optical system using the receiving monochrometer for high-pressure high-temperature device is effective to minimize the error induced by the specimen movement and the shift of the effective diffraction center by the grain growth of the sample. It is also effective for improving the S/N ratio.

Acknowledgements

the calculations in this work. The calculations were carried out by using FACOM M-200 computer system of Nagoya University.

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