Variations of Elastic Constants on Al-Si Alloys by Solid-solutioning under High Pressure*

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Supersaturated solid-solution alloys of the Al-Si system up to 15at%Si were prepared by means of high pressure and high temperature techniques. A cylindrical specimen with a size of $\phi 6 \times 6$ mm for the solid-solutioning treatment was held under the pressure of 5.4 GPa and the temperature of 600°C for 10 hours, and then quenched to room temperature. The elastic constants of thus obtained specimens were measured by a three-dimensional resonance method. Young's modulus E and shear modulus G of the solid solutions were quite smaller than those of the two phase alloys, and they had lower values depending on Si-contents. For example, $E=77.1$ GPa of the two phase Al-10at%Si alloy dropped to $E=62.0$ GPa of the solid solution. Density variations of the specimens were also discussed.

Key Words : Metallic Materials, Heat Treatment, Solid Solution, High Pressure, Elastic Constant, Al-Si Alloy

1. Introduction

Since solute atoms in a solid-solution alloy induce some lattice distortions and internal strains in the alloy matrix, an elastic constant of solid materials decreases in general features. And also the elastic constant is strongly affected by interactions between solvent and solute atoms. It is usually considered that the elastic constant of solid-solution is increased when the binding force between different kinds of atoms is stronger than that between the same kinds of atoms, and it is decreased in the opposite case⁽¹⁾. Such variations of the elastic constants in the solid-solution alloy are long-standing questions. In silver or copper alloys not forming a continuous series of solid-solutions, Young's modulus of almost alloys is decreased by a solid-solutioning though there are a few exceptions. A good correlation between such a lowering rate and an internal strain of the matrix has been revealed by discussions which are concerned with the internal strain caused by size factors of solute atoms⁽²⁾⁽³⁾.

On the other hand, in aluminum alloys it has been reported by Elliott et al.⁽⁴⁾ that Young's modulus was increased by the

solid-solutioning of copper, silver or silicon solute atoms. There was no correlation between the increasing rate of Young's modulus and the size factor in these experiments. Recently, Noble et al.⁽⁵⁾ quote the experiments of Elliott et al. in their study of an Al-Li alloy to develop a new material of high specific moduli, and point out that the variation in the modulus correlates with the deviation from Vegard's law. However, experiments with aluminum solid-solutions are not frequently reported, and especially as a solubility of Al-Si alloy is very limited, the experimental results of Elliott et al. may be considered not accurate and reliable.

So far in the high pressure experiments of Al-Si alloy systems, authors already reported⁽⁶⁾ that the limit of silicon solubility in aluminum was greatly extended from 1.6 at% at 580°C and 0 GPa to over 15 at% at 560°C and 5.4 GPa, and the solid-solution phase could be quenched at a room temperature and pressure. So the method of solid-solutioning under high pressure is applied to increase the silicon contents in Al-Si solid solutions. In the present study, the variations in elastic constants of the Al-Si solid-solutions thus prepared are measured using the resonance method of a small cylindrical specimen, which was fully described in the previous paper⁽⁷⁾. And the variations in lattice constants of the aluminum matrix are also measured by an X-ray diffraction method, and the true density thus obtained is compared with the bulk density which is deduced from buoyancy in water.

2. Experimental Apparatus and Methods

2.1 High pressure solid-solutioning and specimens

The high pressure apparatus and the

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experimental procedures for the solid-solutioning are fundamentally the same as mentioned in the previous paper⁽⁶⁾, so they are briefly described here. The high pressure apparatus is a cubic anvil press (DIA-15), having a pressure vessel volume of $15 \times 15 \times 15 \text{ mm}^3$ composed of six wolfram carbide anvils. These anvils are simultaneously driven by three axial components in which the vertical uniaxial load is divided by wedge actions due to inclined surfaces. The pressure cell assembly for the solid-solutioning is shown in Fig.1. The size of the pyrophyllite as a pressure medium is 20 mm cube including an over size of 30 % for forming the gasket. The carbon heater and the specimen which are insulated by boron nitride (BN) are inserted into the pyrophyllite. The pyrophyllite is baked in atmosphere at 500 °C for 1 hr, and the carbon heater and the BN are preheated in vacuum at 1000 °C for 2 hr. The pressure fixed points of Bi(2.55 GPa), Tl(3.67 GPa) and Ba(5.5 GPa) are used to calibrate the press load, and the temperature is calibrated to the input power by the Pt-Pt13Rh thermocouple.

The testing materials were prepared by casting a mixture of Al-20%Si mother alloy and 99.99 % pure aluminum to a desired composition. After lathe-machined into a cylinder of 6 mm diameter and 6 mm long, the specimen was fully annealed in argon atmosphere at 400 °C for 5 hr. These specimens were solution-treated at high pressure of 5.4 GPa (press load of 8 MN) and temperature of 600 °C (input power of 600 W) for 10 hr, and then quenched to room temperature by shutting off the heating current. The solution-treated specimens were examined by X-ray diffraction experiments, to confirm no silicon precipitate. The specimens were once more machined into a cylinder of $\phi 5.8 \times 5.8 \text{ mm}$ long to measure the elastic constants.

2.2 Measurements of elastic constants

Measurements of elastic constants were performed by three-dimensional resonance of a small cylindrical specimen as reported in the previous paper⁽⁷⁾ in detail. The principles are as follows. The eigen frequencies of a free-vibrating specimen are determined by the size, the density and the elastic constants of the specimen. First, the eigen values are calculated approximately by the Rayleigh-Ritz method in which the size, the density, and the tentative shear modulus G and Poisson's ratio ν are used. Second, the resonance frequencies of the specimen are measured up to higher mode of about 20th, and compared with the calculated values. The eigen value calculations using the elastic constants which were changed little by little, are reiterated until a sufficient agreement is obtained between the calculations and the experiments. Thus the elastic constants are finally determined. The accuracy of the measurements in such a method was about $\pm 0.1 \%$ in G and $\pm 0.5 \%$ in ν . The size of the specimen was measured by a tool projector, and the density was deduced from buoyancy in water by an accurate balance.

3. Experimental Results and Discussions

3.1 Al-10at%Si alloy

The sequence of the present experimental procedures and the results of the elastic constants are shown in Table 2 in the case of the Al-10at%Si specimen. The shear modulus of the cast alloy was slightly increased by the annealing, because of emergence of a perfect two phase alloy of aluminum and silicon. And then by the high pressure solid-solutioning the shear modulus was exceedingly decreased to over 20 %, and on the contrary Poisson's ratio was increased nearly to 10 %. That is to say, the alloy was elastically softened by the treatment. The bulk density of the alloy was increased by solid-solutioning of silicon, and the lattice constant of the aluminum matrix was simultaneously lowered by about 0.4 % from the value of $0.049 \times 10^{-10} \text{ m}$ in the pure aluminum, i.e., the lattice was constricted. The variation rate of the lattice constant a per atomic fraction c , i.e., the lattice strain ϵ_a around the solute atom is

$$\epsilon_a = (1/a) (\partial a / \partial c) \\ = -0.038 \dots \dots \dots (1)$$

This value is slightly smaller than the experimental value -0.043 of Axon et al.⁽⁸⁾ up to 1 at%Si, but agrees with the value -0.038 of Itagaki et al.⁽⁹⁾ by the splat cooling technique. The elastic constants and the density are almost restored to the initial state by the last recovery. Further developments of the recovering process will be reported on another occasion.

Table 1. The contents of Al-20%Si mother alloy.

Si	Fe	Cu	Al
19.8	0.25	0.01	bal.

Fig.1. The high pressure cell assembly for the solid-solutioning.

Table 2. The experimental results of the elastic constants and the treatment conditions in the Al-10at%Si alloy.

Heat Treatment	Density (g/cm^3)	Shear Modulus (GPa)	Poisson's Ratio	Si Pre- cipitates	Lattice Constant (10^{-10}m)
1. Cast (about 800 °C)	2.662	28.41	0.338		
2. Annealing (400 °C, 5 hr)	2.653	28.88	0.334	Yes	
3. High Pressure Solid Solution- ing (5.4 GPa, 600°C, 10 hr)	2.743	22.77	0.361	No	4.034*
4. Recovering (400 °C, 5 hr)	2.654	27.60	0.330	Yes	

* Mean Value on 3 Specimens

Table 3. The experimental values of the bulk density and the elastic constant, and the treatment conditions of all specimens.

Specimen	Cast (about 800 °C)			Annealing (400 °C, 5 hr)			High Pressure Solid Solutioning (5.4 GPa, 600 °C, 10 hr)		
	Density (g/cm^3)	Shear Modulus (GPa)	Poisson's Ratio	Density (g/cm^3)	Shear Modulus (GPa)	Poisson's Ratio	Density (g/cm^3)	Shear Modulus (GPa)	Poisson's Ratio
Pure Al	2.699	26.18	0.345	2.701	26.26	0.342	2.705	26.26	0.345
Al-1at%Si	—	—	—	2.687	26.17	0.343	2.699	25.75	0.345
Al-5at%Si	2.681	26.54	0.330	2.674	27.17	0.338	2.714	24.54	0.353
Al-10at%Si	2.662	28.41	0.338	2.653	28.88	0.334	2.743	22.77	0.361
Al-15at%Si	2.644	29.85	0.331	2.637	30.09	0.329	2.754	21.81	0.368

Fig.2. The variations of the shear modulus G and Poisson's ratio ν .

3.2 Variations of elastic constants

The experimental results about the shear modulus G and Poisson's ratio ν of the pure aluminum, and Al-1, 5, 10, 15at%Si are shown in Fig.2. The numerical values and the bulk densities are also shown in Table 3. In the annealed two-phase state, G increases linearly with the atomic fraction c of silicon, and the gradient is $\partial G/\partial c = 29$ GPa. Poisson's ratio ν decreases in the gradient $\partial \nu/\partial c = -0.11$. In the high pressure solid-solutioning state, while G decreases with c in the gradient $\partial G/\partial c = 32$ GPa, and ν increases in $\partial \nu/\partial c = 0.16$. As can be seen from the figure, both G and ν of the pure aluminum are never varied by the high pressure treatment. It is, therefore, considered that such enormous variations of elastic constants are caused by solid-solutioning of silicon atoms.

Thus the variation of elastic shear modulus G with a solid-solutioning silicon content c is

$$(1/G)(\partial G/\partial c) = -1.23 \quad (2)$$

in the present experiments. Zener⁽¹⁰⁾ has introduced a next expression for the variation of G due to an internal strain energy of solid-solution, using hypotheses of elastic continuum and the thermodynamics.

$$(1/G) (\partial G/\partial c) = 4(\epsilon_a)^2 (\partial G/\partial T) / Nk \dots \dots \dots (3)$$

where ϵ_a is the lattice strain, $\partial G/\partial T$ the temperature derivative of G , N the atomic number per unit volume, and k the Boltzmann constant. By substituting the existing value⁽¹⁰⁾ -0.014 GPa/°C of the temperature derivative of G and the present lattice strain of Eq.(1) into Eq.(3), we obtain

$$(1/G) (\partial G/\partial c) = -0.097$$

This value is less than 1/10 of the present experimental result. It is, therefore considered that contributions of the internal strain to the decreasing of G due to silicon solution in aluminum are very small, and the main part of that is caused by Al-Si interaction parameters. As Al-Si alloy system is a simple eutectic system, in which there is no solid-solution in silicon side and no intermetallic phase, the interaction parameters may be repulsive. So it is qualitatively understood that the elastic constants are decreased by the repulsive potentials.

3.3 Variations of bulk density

The bulk density of the two-phase specimens decreases linearly with the silicon content c as shown in Fig.3. A precipitate silicon has a diamond structure with a lattice constant $a=5.428 \times 10^{-10}$ m, of which the atomic volume is larger than that of aluminum of a face centered cubic structure $a=4.049 \times 10^{-10}$ m. The true density (a broken line in the figure) deduced from these lattice constants agreed well with the present measurements. On the contrary, the bulk density in the high pressure solid-solutioned specimen increased with the silicon content. This was in a good agreement with the true density (a solid line in the figure) which was deduced from the variation of the matrix lattice constant by the silicon solutioning. In the present speci-

Fig.3. The variations of the bulk density (a broken line and a solid line are the density of the two-phase and the solid-solution, respectively).

mens of the casting or the high pressure solid-solutioning, therefore, it is considered that there are not so much impurity, lattice defect, void, and deviation of concentration which are detectable by a variation of the density.

3.4 Young's modulus of two-phase alloy

As Young's moduli have been measured well so far in the experiments, Young's modulus E deduced from G and ν in the present experiments of two phase alloys are shown in Fig.4. The experimental values of cast alloys by Dudzinski et al.⁽¹¹⁾ were smaller than those in the present experiments of the annealed alloys as a whole, and our value of the annealed alloy at 5 at%Si agreed with their value. As the silicon solubility limit is 1.6 at% even under the atmospheric pressure, the cast alloys are not a perfect two-phase system, but are supposedly a solid-solution with a small quantity of silicon. In general, the elastic constants of a polycrystalline two-phase alloy can be estimated in the upper and lower boundary values from the elastic constants of each single crystal⁽¹²⁾. These values were estimated using the existing single crystal elastic constants of aluminum and silicon⁽¹⁰⁾, and the results were shown in the same figure as a dotted line (upper bound) and a two-dotted line (lower bound). It is obvious from the figure that the present experiments agree with the lower boundary values which are estimated under the condition of a homogeneous internal stress.

3.5 Young's modulus of the solid-solution

The variation of the elastic modulus with silicon contents in the specimen after the solid-solutioning is shown in Fig.5, comparing with the results of Elliott et al.⁽⁴⁾ Young's moduli of the present results decrease with silicon content c in the ratio of about 0.8 GPa/%Si.

Fig.4. The variations of Young's modulus in the two-phase alloys (a dotted line and a two-dotted line are estimated values for the upper bound and the lower bound, respectively, and a broken line indicates the experimental values about the cast alloys by Dudzinski).

Fig.5. The variations of Young's modulus in the solid-solutions.

Its derivative to 10 at%Si, which is slightly smaller at 15 at%Si, is

$$(1/E)(\partial E/\partial c) = -1.14$$

On the contrary, in the results of Elliott et al., E very much increased with c , and its derivative was

$$(1/E)(\partial E/\partial c) = 8.7$$

Such a large variation was not reasonable, even though the silicon had been precipitated in the specimen. In addition, Young's moduli as a whole were still more increased by about 4 % through an aging heat treatment after solid-solutioning. If we take notice of a given content of Si, Young's modulus is decreased by the solid-solutioning as a result. This agrees with the present experiments. It is, however, considered that a sufficient variation of Young's modulus to be detected is not developed, because the solubility of silicon is very limited by the solid-solutioning under the atmospheric pressure.

4. Conclusions

The variation of the elastic constants with the solid-solutioning silicon in aluminum was measured in specimens containing silicon up to 15at%. The specimens were prepared by the high pressure solid-solutioning method. The conclusions are

obtained as follows.

(1) The elastic constants are decreased by the silicon solid-solutioning. In the case of the Al-10at%Si alloys, Young's modulus decreased from $E=77.1$ GPa of the two-phase precipitated specimen to $E=62.0$ GPa of the solid-solutioning one, and the derivatives of G and E by silicon content c were

$$(1/G)(\partial G/\partial c) = -1.23$$

$$(1/E)(\partial E/\partial c) = -1.14$$

respectively.

(2) On account of the above mentioned decrease of the elastic constants, the contributions of the internal strain energy turned out as small as 1/10 of a whole.

(3) The elastic constants of the two-phase alloy were nearly equal to the lower boundary values deduced from the single crystal elastic constants, and these values generally agreed with the existing experiments of the cast alloys.

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