JOURNAL OF MATERIALS SCIENCE 31 (1996) 3309–3313

Elastic moduli of Al–Li alloys treated at a high pressure of 5.4 GPa

K. SAKAI, A. MATSUMURO
Department of Mechanical Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan
M. SENOO
Department of Mechanical Engineering, Mie University, Kamihama-cho, Tsu 514, Japan

The elastic moduli of high pressure treated supersaturated Al–Li solid solutions were measured. An interesting elastic behaviour was observed, in that, the bulk modulus decreased with an increase in the lithium content, whereas the Young's modulus and shear modulus increased. In order to clarify this property, we investigated the compressibility of the Al–Li supersaturated solid solutions prepared by high-pressure solid-solidification by high-pressure Synchrotron X-ray diffraction. The obtained pressure–volume relations were fitted to Birch's equation of state. The calculated bulk moduli were lower than those of pure Al at a reduction of about 0.6 GPa per mol % Li. The temperature dependence of the elastic modulus for those supersaturated solid solutions was also measured, and it was found that the trend in the variation of the elastic modulus against the lithium concentration was maintained in the temperature range of 5–290 K. Therefore the attractive relationship between the bulk modulus and Young's modulus was demonstrated to be intrinsic.

1. Introduction

Al–Li alloys are well known for their high specific modulus and use in aerospace applications. In a previous publication, we investigated the high pressure Al–Li phase diagram, and observed the extension of the maximum solid solubility for Li from 15 mol % at atmospheric pressure to 20 mol % at 5.4 GPa and the elevation of the eutectic temperature from 870 K to 1070 K [1]. The extension of the Li solid solution suggests that an alloy produced at high pressure would have a higher modulus and a lower density. In this study we investigate the elastic modulus of Al–Li alloys obtained by high pressure treatments. In particular the Young's modulus E, the shear modulus G and the bulk modulus B were measured using the resonance method. Contrary to an expected increase in the elastic moduli of an alloy, with an increase in the Li concentration we found an increase in the Young's modulus and the shear modulus but a decrease in the bulk modulus. In order to clarify this curious elastic behaviour we further probed the bulk modulus by investigating the relationship between the atomic volume and pressure using high pressure X-ray diffraction (XRD) techniques. In general, X-ray diffraction experiments performed in a high-pressure environment require a long time since the weak intensity of the diffracted beam requires a long count period to enable good enough counting statistics to differentiate the peaks from background noise. In the present study, we used the synchrotron radiation light source at the national high energy physics laboratory (KEK), thus the measurements could be done within a shorter time frame and with greater accuracy than with a conventional X-ray diffraction approach. Since an understanding of the thermal dependence of the elastic modulus is crucial we have measured changes in the elastic modulus of the alloy as a function of temperature. It was observed that the previously mentioned decrease in the bulk modulus was an intrinsic property at all investigated temperatures.

2. Experimental procedure

Specimens were prepared by the high pressure solid solidification method described in the previous paper [1]. Fig. 1 shows the phase diagram for Al–Li at 5.4 GPa that we reported, and the conditions for the solid solution between the constituent metals were chosen from this diagram. We prepared alloys that contained 5, 10 12.5, 15 and 17.5 mol % Li, whose phase composition was checked by X-ray diffraction techniques. All the specimens were identified as being single-phase products and these alloys were then used in the following experiments.

2.1. Measurement of the elastic modulus

Specimens treated under high pressure were very small in size (typically 6 mm dia. × 6 mm) so reproducible measurements could not be expected using the conventional method. The three-dimensional vibration method was employed and accurate and reproducible

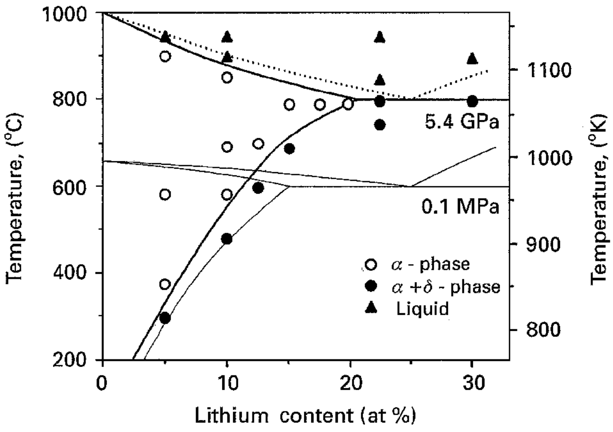

Figure 1 High-pressure phase diagram of Al-rich Al–Li alloy at a pressure of 5.4 GPa [1]. The maximum solid-solubility of Li in Al is extended from 15 mol % up to 20 mol % by the use of a high-pressure, and also the eutectic temperature is raised from 873 K to 1073 K.

measurements were easily carried out in a relatively short time. Moreover, the measuring equipment is small enough to allow insertion into high or low-temperature devices, thereby facilitating measurement of the temperature dependence of the elastic moduli [2].

A brief review of the method is now presented. The resonance frequencies of a specimen correspond to its size, shape, density and elastic moduli. Generally, the resonance frequencies can be calculated using the size and density (which can be readily measured) and elastic moduli, but the reverse operation is impossible, i.e., the elastic moduli cannot be calculated analytically from the resonance frequencies. Therefore, we first assume a specimen to be homogeneous and isotropic and then postulate two independent elastic moduli. By using these parameters, numerical calculations are made and the calculated and measured resonance frequencies are compared. Thus, the appropriate elastic moduli are fixed so as to give the minimum differences between them. The accuracy of the obtained elastic constants is within a few percent, as estimated by the standard deviations of the results for each resonance frequency.

Hence, the shear modulus G and Poisson's ratio ν of the polycrystalline samples were determined simultaneously with a measurement accuracy of about $\pm 0.1\%$. The sample density was measured by Archimedes method using water as the immersion fluid. The Young's modulus E and bulk modulus B can be deduced from G and ν by use of Equations 1 and 2 assuming the isotropic material assumption is applicable and it is well known that aluminum alloys satisfy this requirement.

$$E = 2G(1 + \nu) \tag{1}$$

$$B = \frac{2(1 + \nu)}{3(1 - 2\nu)} G \tag{2}$$

2.2. High-pressure X-ray measurement

In previous measurements, it was observed that in the Al–Li alloy, the Young's modulus increased with the addition of lithium, whereas the bulk modulus surprisingly decreased. In order to clarify this feature, we investigated the compressibility of the alloys using a high-pressure X-ray diffraction method. A schematic illustration of the experimental apparatus (MAX80 at KEK) is shown in Fig. 2. A synchrotron radiation light source has the significant advantages over conventional X-ray sources of extremely high intensity, low dispersion and homogeneous white light. When applied to high-pressure experiments, synchrotron radiation assures shorter measuring times over the conventional method since there is a high intensity for the measuring diffraction beam. Thus, *in situ* observations of the specimen under high-pressure may be made with high accuracy and efficiency. The basic procedure for generating high pressures is essentially the same as discussed in the previous paper, although in these experiments the transmitting pressure medium consisted of a mixture of boron and epoxy resin which is transparent to X-rays , and a NaCl pressure marker was also inserted. Specimens were Al–5, 10 and 15 mol % Li alloys previously solidified under high pressure, and they were compressed to 100 N (load from the press) in 5 or 10 N steps, the

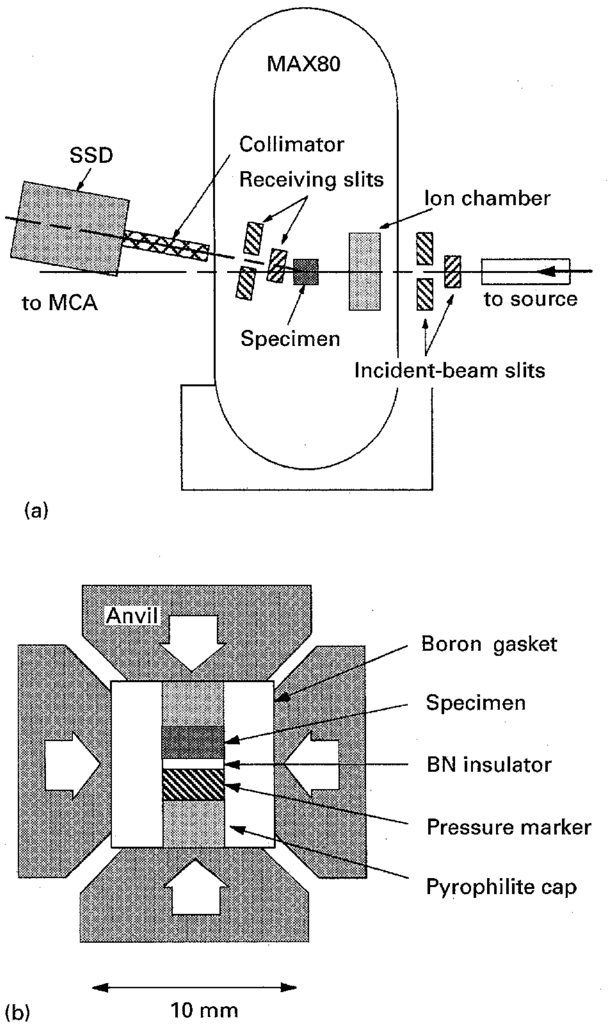

Figure 2 (a) Schematic diagram of the high-pressure X-ray diffraction apparatus (MAX80) at the X-ray beam line of the TRISTAN accumulation ring at the National Laboratory for High Energy Physics (KEK). (b) Sample assembly for high-pressure X-ray diffraction experiments.

measurements of the lattice constants of both the specimen and the NaCl pressure marker were carried out at every step in the load. The actual sample pressure was determined from the lattice constants of the NaCl by Decker's equation of state [3]. The bulk modulus of the specimen was determined from Birch's equation of state using the resultant pressure–volume relation

$$P = \frac{3}{2} B_0 \left\{ \left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3} \right\} \quad (3)$$

Where, B_0 means the bulk modulus at atmospheric pressure and V and V_0 are the atomic volume of the specimen at a pressure of P and at atmospheric pressure, respectively. This equation was derived from thermodynamic calculation at limited strain conditions and is valid for the calculation of B from our experimentally observed data.

2.3. Temperature dependence of the elastic modulus

The temperature dependence of the elastic moduli in Al–5, 10, and 15 mol % Li alloys was measured using a liquid He cooled cryostat as previously discussed [4]. The Al–Li solid solution alloy starts to decompose at a relatively low temperature, as we will present in a separate report, so the measurements were performed from 295–5 K.

3. Results and Discussion

3.1. Variation of the elastic modulus versus Li concentration

Figs 3, 4 and 5 show the variation with Li concentration of the Young's modulus E, shear modulus G and bulk modulus B, respectively. Noble *et al.* [5] pointed out that the increase in Young's modulus for Al–Li solid solutions is rapid over the first 5 mol % of Li addition though thereafter the rate of increase falls due to the precipitation of Al_3Li [5]. In the present experiment, this feature is not evident in Figs 3 and 4. Thus, this system shows a continuous increase in E and G with the solute concentration. However, the bulk modulus of the solid solutions significantly decreases with increasing solute concentration, having a slope of -0.51 GPa per mol % Li. This elastic property is a unique phenomenon in the aluminum solid solutions. The moduli of Al–Cu [6], Al–Si [7] and Al–Ge [8] have the same trend in each modulus with solute concentration. The decrease in the bulk modulus with solute concentration is discussed in more detail in the next section.

Fig. 6 shows the specific moduli for E as a function of the Li content. The elastic modulus of the solid solution containing 17.5 mol % Li is 40% higher than that for Al. This level is comparable to the fibre reinforced plastics (FRP) value (40 GPa kg^{-1} cm^{-3}). This property is worth noting for practical applications [9]. Furthermore, higher performance can be obtained by the thermal processing.

The attractive increase in the maximum solid solubility using high pressure treatment is expected to significantly improve the physical and mechanical properties of Al–Li alloys.

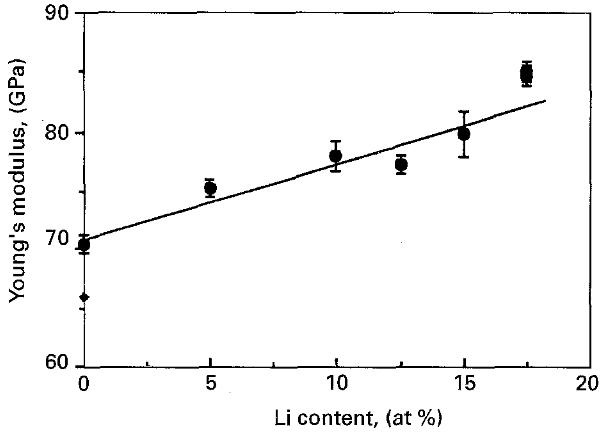

Figure 3 Variation of Young's modulus with respect to lithium atomic concentration.

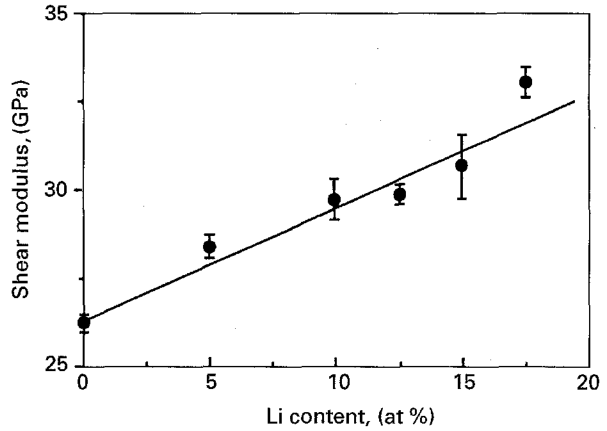

Figure 4 Variation of shear modulus with respect to lithium atomic concentration.

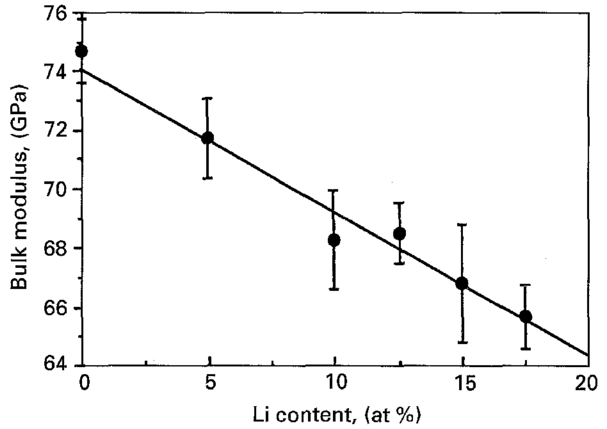

Figure 5 Variation of bulk modulus with respect to lithium atomic concentration.

3.2. Variation of the bulk modulus

In this section we investigate the compressibility of the solid solutions.

Fig. 7 shows a Synchrotron radiation XRD pattern of Al–5 mol % Li alloy which contains many

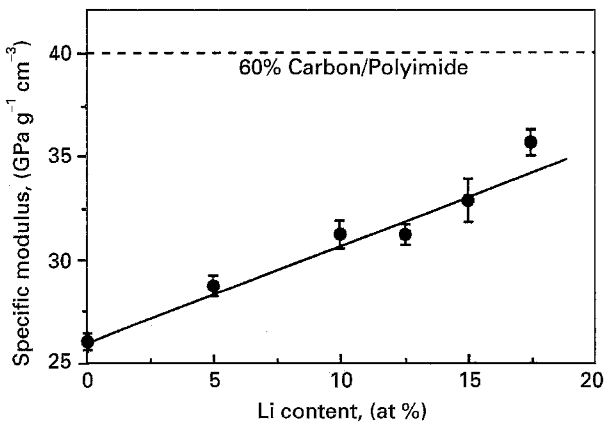

Figure 6 Variation of specific modulus with respect to lithium atomic concentration.

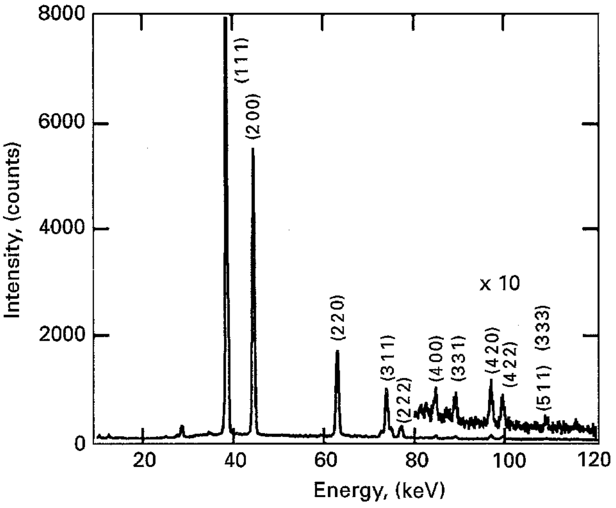

Figure 7 Energy dispersive X-ray diffraction pattern of Al–5 mol % Li at 2.8 GPa and 295 K.

clear diffraction peaks. The advantage of synchrotron radiation is evident from this figure. The XRD profile was fitted to a Gaussian distribution and *d*-spaces were calculated. The lattice constants were obtained by the least squares method. The resultant pressure–volume relations are shown in Fig. 8. It is possible that an uneven pressure is exerted on the specimen during a high-pressure experiment using a solid pressure medium. For the case of Al, an anisotropic compression tends to produce stacking faults. This results in the (200) plane becoming more compressed than other crystallographic planes. This is reflected in a large variation in the *d* spacing for the (200) plane [10]. Fig. 9 shows the variation in various *d*-spacings in our experiment. No catastrophic changes in the *d* spacings were observed and thus we conclude that the compression was uniform.

The bulk modulus of Al–Li alloys and pure Al calculated in this manner are listed in Table I, which clearly shows the decrease of bulk modulus with increasing lithium concentration. The results are in good agreement with the results from the resonance method, in that the addition of lithium is observed to decrease the bulk modulus whilst increasing the Young's modulus and the shear modulus.

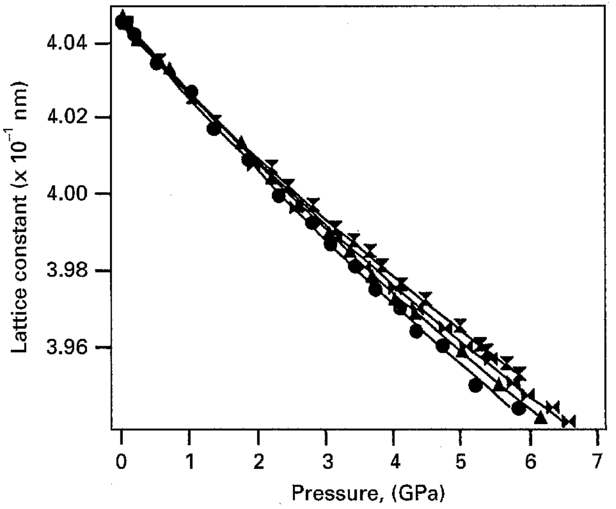

Figure 8 Resultant pressure–volume relations of; (⧗) pure Al, (⧓) Al–5 mol% Li, (▲) Al–10 mol % Li and (●) Al–15 mol % Li alloys. The lines were fitted with Birch's equation of state.

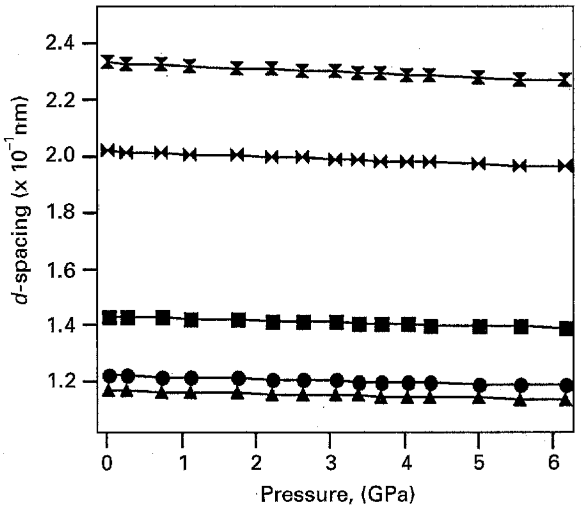

Figure 9 Variation of *d*-spacings of Al-5, 10 and 15 mol% Li alloys versus pressure. Bragg reflections investigated were; (⧗) (111), (⧓) (200), (■) (220), (▲) (222) and (●) (311).

TABLE I The bulk moduli in Al–Li solid solutions.

Specimen	Bulk modulus (GPa) P–V relation	 Resonance method
Al	74.8	74.7
Al–5 mol % Li	69.5	71.5
Al–10 mol % Li	66.8	67.9
Al–15 mol % Li	64.5	66.9

3.3. Temperature dependence of the elastic modulus

These variations in the elastic moduli in Al–Li solid solution mentioned above are measured at room temperature (293 ± 1 K). The possibility must be considered that the unique property of the bulk modulus may be a particular aspect at this temperature. Senoo *et al.* [7, 8] pointed out that the shear modulus of an aged Al–Cu alloy, is higher than that of the solid

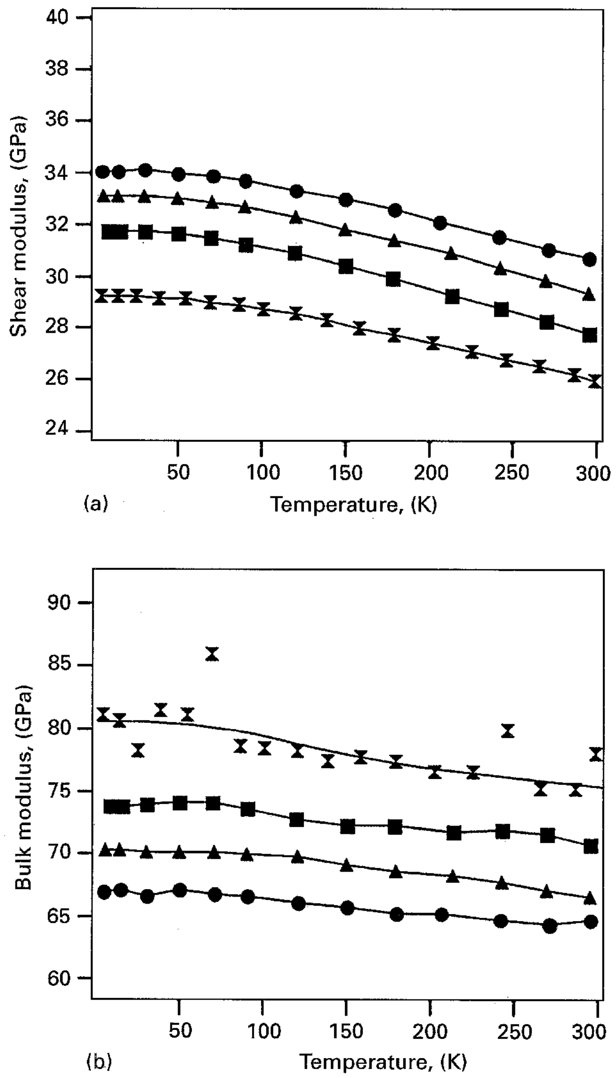

Figure 10 Temperature dependences of; (a) G and (b) B in the Al–Li solid solutions at the range of 295–5 K. The elastic moduli were measured using the resonance method. The samples used for both measurements were (⧗) pure Al, (■) Al–5 mol % Li, (▲) Al–10 mol % Li and (●) Al–15 mol % Li.

solution at room temperature, although both showed virtually the same value at 120 K [6].

Fig. 10 shows the resultant temperature dependence of G and B in Al–Li solid solution from room temperature to 5 K. In this temperature range, the Young's modulus rose together with the Li concentration whilst the bulk modulus decreased, so the changes in elastic modulus tended to be negligible.

Therefore, one cannot easily maintain that Al–Li alloy is more "rigid" than the other aluminum alloys, because it has a higher E and G but lower B value than the other alloys.

4. Conclusions

The elastic properties of high-pressure solid solidified Al–Li alloys were investigated. The variation of the elastic modulus versus Li concentration in the alloy is linear up to 17.5 mol % Li. The Young's modulus and shear modulus increased at the rate of 0.69 GPa per mol % Li and 0.28 GPa per mol % Li, respectively whilst the bulk modulus decreased by − 0.51 GPa per mol % Li. To verify this curious phenomena, the pressure–volume relation was investigated by using high pressure synchrotron X-ray diffraction, and the resultant bulk modulus was in good agreement with previous results. Finally, the temperature dependence of the elastic modulus for those supersaturated solid solutions was also measured and it was found that the trend in the variation of the elastic modulus against the lithium concentration was maintained in the temperature range 5–290 K. Therefore the relationship between the bulk modulus and Young's modulus was demonstrated to be intrinsic.

Acknowledgments

We would like to thank Dr. T. Kikegawa of KEK for supporting the high pressure X-ray diffraction experiment and Mr. Y. Masanaka of Nagoya university for preparing the high pressure cell. This study was also made possible in part by the support of the Light Metal Foundation.

References

1. A. MATSUMURO, K. SAKAI and M. SENOO, *J. Mat. Sci.* **28** (1993) 6567.
2. M. SENOO, T. NISHIMURA and M. HIRANO, *Trans Jpn. Soc. Mech. Eng.*, **50** (1984) 440 (in Japanese).
3. D. L. DECKER, *J. Appl. Phys.* **42** (1971) 3239.
4. A. MATSUMURO, T. NAGASAKA and M. SENOO, *JSME Int. J. Ser. I* **36** (1992) 220.
5. B. NOBLE, S. J. HARRIS and K. DINSDALE, *J. Mat. Sci.* **17** (1982) 461.
6. M. SENOO and T. HAYASHI, *JSME Int. J. Ser I* **31** (1984) 664.
7. M. SENOO, T. NISHIMURA, I. KONDO and K. MIYASHITA, *ibid.* **28** (1985) 1809.
8. M. SENOO and A. MATSUMURO, *J. Soc. Mat. Sci. Jpn* **37** (1987) 126. (in Japanese)
9. J. W. MARTIN, *Ann. Rev. Mater. Sci.* **18** (1988) 101.
10. H. MII, I. FUJISHIRO and M. SENOO, *Memo. Fac. Eng. Nagoya Univ.* **28** (1976) 191.

Received 4 July 1994
and accepted 15 December 1995