Structural Analysis of Molten Bi-Pb Alloys near Their Liquidus Temperatures

By Naoshi Matsuno*, Hiroaki Nakayama** and Masayuki Momiuchi***

Energy scanning X-ray diffractometry was used for studying the structure of Bi-Pb liquid alloy. All the measurements were made at 10 K above the liquidus temperature. Results were analyzed by defining two kinds of the coordination numbers, N_i and N_m . Both N_m and N_i vary very much at border of eutectic composition. The values of N_m were 6.6 to 7.0 for pure Bi to 44 at% Pb, and 11.0 to 11.2 for 54 at% Pb to pure Pb, and they are very close to the coordination number of primary crystal, respectively, in hypoeutectic and hypereutectic.

(Received January 27, 1990)

Keywords: X-ray measurement, energy scanning diffractometry, liquid structure, bismuth-lead alloy, coordination number

I. Introduction

Coordination number N is an important quantity to describe the structure of liquid metals, and there have been reported many reports on its temperature dependence, etc. Since typical metals having fcc or bcc crystal structure among these metals take large coordination number even after melting, discussion has been made through a model of random spaced hard spheres⁽¹⁾⁻⁽³⁾ based on packing density. It has been reported, however, that metals of lower symmetry in the solid state such as Cd, Sn and Bi take a lower coordination number than the above metals even after melting, and take one close to that of solid structure⁽⁴⁾⁽⁵⁾ especially near the melting point. Recently, there are an attempt to directly apply the coordination structure of "4+2" for the solid state to the analysis of Sn⁽⁶⁾ in the liquid state and an interesting report on a Fe-Si⁽⁷⁾ liquid alloy with regard to the composition dependence of $S(Q)$, $g(r)$ and N , having almost the same characteristics up to 40 at% Si as those of pure Fe.

As in the above alloy, we investigated the composition dependence of coordination number N and pair distribution function $g(r)$ in a Bi-Pb liquid alloy. The reasons for the selection of the material are as follows: (1) Bi, one constituent of the alloy, has subsidiary peaks in its $g(r)$ curve⁽⁸⁾⁻⁽¹⁰⁾ at the right side of the first peak, and the structure of liquid Bi supercooled has been discussed on the basis of the temperature dependence of this subsidiary peaks⁽¹¹⁾; (2) contrary to Bi, the $g(r)$ curve for Pb does not have the subsidiary peak and oscillates monotonous-

ly⁽¹²⁾, and (3) the $g(r)$ curve of the alloy, composed of these two kinds of metal, is expected to show a subsidiary peak varying with composition similarly to the results of supercooled Bi.

II. Experimental

The measurements were made using energy scanning X-ray diffractometry⁽¹³⁾⁽¹⁴⁾. The details of the equipment and method of analysis are described in the previous reports⁽⁸⁾⁽¹¹⁾. The effective energy range of the used continuous X-ray was 17 to 47 keV, and the incident angles, θ_i , were four kinds of 5°, 7°, 9° and 16°. The scattered X-ray data obtained with each incident angle were divided, according to energy, into 1024 divisions, and recorded with a multi-channel pulse-height analyzer. These data contain irregular pulse-like noise. In order to improve the S/N ratio of signal in analysis, each data was filtered off for high frequency range pulses by use of the Fourier transformation (FT) method, and to smoothing. The atomic scattering factor for the alloy, f_{alloy} , was approximated by the following equation, because the atomic numbers of Pb and Bi are close to each other,

$$f_{\text{alloy}}^2 = f_{\text{Pb}}^2 \cdot x + f_{\text{Bi}}^2 \cdot (1 - x)$$

where x is the concentration ratio of Pb to Bi. The normalization for the intensity of scattered X-rays was done using the Krogh-Moe-Norman method⁽¹⁵⁾⁽¹⁶⁾. In the case of $Q < 1.3 \text{ \AA}^{-1}$, the $S(Q)$ was extrapolated smoothly to zero. The process of determining $S(Q)$ is the same as that previously reported. The IFT method⁽¹⁷⁾ was used to minimize the ghost arising from normalization, removal of background, termination effect, etc., and the ripple occurred in the domain of small r in the pair distribution function. The specimen was prepared from of 99.9999 mass% Pb ingot and Bi ingot. The alloy compositions were expressed by the ratio of Pb to Bi in at%, and they were 0, 34, 44 (eutectic), 54, 62, 70 and 100. The solid rounds in the phase diagram of the Bi-Pb binary alloy of Fig. 1 show the compositions and the temperatures

* Department of Physics, Faculty of Science, Science University of Tokyo, Shinjuku-ku, Tokyo 162, Japan.

** Graduate Student, Science University of Tokyo. Present address: Central Research Institute, Mitsubishi Metal Corporation, Kitabukuro, Omiya 330, Japan.

*** Science University of Tokyo. Present address: Technical Research Institute, Topcon Corporation, Itabashi-ku, Tokyo 174, Japan.

Fig. 1 The phase diagram of the Bi-Pb alloy system. Rounds denote the compositions of samples and their temperatures of measurements.

measured, respectively, in the experiment. All the measurements were made at 10 K above the liquidus temperature. The specimen and the furnace were placed in a vacuum of $\sim 10^{-4}$ Pa. Prior to the measurement, each specimen was heated to 613 K, held at the temperature for 1 h, and then slowly cooled to the temperature of measurement. The density of the liquid alloy at each measurement temperature was determined by proportional calculation, using the value obtained by the Archimedes' method for Bi and eutectic composition, 0.0289×10^{30} and 0.0297×10^{30} atoms $\cdot$ m $^{-3}$, respectively, and the value for Pb from reference⁽¹⁸⁾, 0.0300×10^{30} atoms $\cdot$ m $^{-3}$.

III. Results and Discussions

The $S(Q)$ at 10 K above the liquidus temperature for each composition are shown in Fig. 2. The numbers in the figure show the at% ratio of Pb to Bi. The $S(Q)$ curves at Bi and Pb coincide well with the previous data⁽¹⁴⁾⁽¹⁹⁾. And, a small peak observed with Bi at the right side of the first peak becomes smaller as the Pb concentration increases, and approaches rapidly to the curve of Pb as the eutectic concentration of 44 at% is surpassed. Figure 3 shows the pair distribution function $g(r)$. The curve which showed subsidiary peaks for pure Bi has its height of subsidiary peaks decreased as the Pb concentration increases. Especially when the composition varies from hypoeutectic to hypereutectic, the subsidiary peaks change very much. After that, the subsidiary peaks decrease rapidly, and is not observed for pure Pb.

Our experimental results were analyzed by defining two kinds of coordination numbers. The one is the main coordination number N_m , the value of which is obtained by integration of the radial distribution function, $4\pi r^2 \rho_0 g(r)$, up to the first minimum position beyond the first peak, and the other is the total coordination number N_t , which is the value obtained by integration of radial distribution function up to the lowest position r between the first and the second peak. Here, ρ_0 is the average number density of atoms. The composition dependences of N_m and N_t are shown in Fig. 4 and 5, respectively. The coordination number N_m can be grouped into two sets of values with regards to composition, i.e. they are 6.0 to 7.0 for pure Bi to the eutectic composition, and 11.0 to 11.2 beyond the eutectic composition to pure Pb. The results coincide very well with the report of Marcus⁽²⁰⁾. In

Fig. 2 Structure factor $S(Q)$ at 10 K above liquidus temperature for each composition. Probable error of $S(Q)$ curve were within $\pm 2.0\%$ including statistical and unavoidable errors resulting from experimental conditions.

Fig. 3 Pair distribution functions $g(r)$ for molten Bi-Pb alloys at 10 K above their liquidus temperatures. Ripple occurred in the domain of small r in $g(r)$ was minimized using the IFT method.

Fig. 4 Composition dependence of the main coordination number N_m for Bi-Pb liquid alloys. The value of N_m is obtained by integration of RDF up to the first minimum position beyond the first peak.

Fig. 5 Composition dependence of the total coordination number N_t and mean atomic density ρ_0 for Bi-Pb liquid alloys. The value of N_t is obtained by integration of RDF up to the lowest position r between the first and the second peak.

contrast with N_m , the N_t values are 17.8–17.9 for hypoeutectic compositions, and, on the other hand, they are 11.0–12.5 for hypereutectic compositions, very close to those of N_m (Fig. 5). Thus, both N_m and N_t vary very much at the border of eutectic composition⁽⁷⁾. The number density of atoms ρ_0 (atoms $\cdot$ m⁻³) in this alloy increase, however, monotonously from 0.0289×10^{30} for Bi to 0.0300×10^{30} for Pb. Therefore, the rapid change in coordination number must arise only at several atomic distances. The large N_t values at the hypoeutectic side arise, because subsidiary peak seen at the tail of the first peak does not separate completely from the second peak side, as seen in Pb. The results suggest that as in pure Bi

around the melting point, there exist superimpositions^{(21)–(23)} of atom coordination of two or more, at the hypoeutectic side of the Bi-Pb alloy, and it appears as “a superimposition of the radial distribution function” as seen, for example, in the analysis by Momiuchi⁽¹¹⁾. On the other hand, at the hypereutectic side, the Pb-like atom coordination predominates. The fact that the numbers of the nearest neighbor atoms of pure Bi and pure Pb are 3 + (3) and 12 in the solid state, respectively, and an example of the analysis for liquid Sn⁽⁶⁾, suggests that some kind of correlation exists between the liquid structure of the Bi-Pb alloy and the alloy's atom coordination in the solid state. With regard to the factors for the change like this, attention has been paid at first to the radial distribution of the primary crystal structure crystallizing at each liquidus temperature, and secondly to the covalent bond character of semi-metal Bi. As is well known, the structure of α -Bi, being the primary crystal at hypoeutectic, has neighbor atoms in the number of 3 + (3), and on the other hand, its structure at the hypereutectic side has quasi-stable hcp⁽²⁴⁾ (ϵ -phase) and fcc (β -Pb) structures. Therefore, even when it is in the molten state at the hypoeutectic side, if the covalent component remains as a short range order, the coordination number according to it could be observed. It is also reported that the volume of Bi decreases 3% upon melting⁽²⁵⁾, and that around the melting point the two kinds of structures having a strong interaction at a round nearest neighbor atom's distance and having the simple packing as seen generally in liquid metals at high temperatures. Integrating these, the hypoeutectic side can be considered to have mixing at a appropriate ratio of the states of coordination of 3 + (3) and 12. Since the hypereutectic side has both N_m and N_t at approximately 12, the close-packed structure could be easily imagined. The structure of liquid certainly differs from that in the crystallized state, but its coordination number is in the presented state. For example, from the calculation results of microclusters⁽²⁶⁾, icosahedron can be claimed as a short range order structure satisfying the same coordination number as the fcc structure. Similarly, the hypoeutectic side is also believed to have clusters⁽²⁷⁾ with the covalent bond character.

IV. Conclusions

Using energy-scanning X-ray diffractometry, the Bi-Pb liquid alloy was analyzed. The measurement was conducted at 10 K above the liquidus temperature for each composition. From the obtained RDF, the two kinds of coordination numbers of N_m and N_t were estimated. Their curves vary very rapidly, with composition, at the eutectic composition. The values of N_m were 6.6 to 7.0 for pure Bi to 44 at% Pb, and 11.0 to 11.2 for 54 at% Pb to pure Pb, and they are very close to the coordination number of the primary crystal, respectively, in hypoeutectic and hypereutectic. On the other hand, the N_t is larger at the hypoeutectic side, and is $N_m \sim N_t$ at the hypereutectic side. These results show that the atom coordination, similar to the one for the primary crystal crystallizing at

the liquidus temperature, predominates in the liquid alloy near the liquidus temperature, as pure liquid Bi⁽¹¹⁾.

REFERENCES

- (1) M. R. More and P. Pal: *Adv. Phys.*, **20** (1971), 161.
- (2) F. H. Stillinger and R. A. Lavolette: *J. Chem. Phys.*, **83** (1985), 6413.
- (3) Xian-Wu Zou, Zhun-Zhi Jin and Ya-Jun Shang: *Phys. Stat. Sol. (b)*, **139** (1987), 365.
- (4) K. Furukawa, B. R. Orton, J. Hamor and G. I. Williams: *Phil. Mag.*, **8** (1963), 141.
- (5) P. Lamparter and S. Steeb: *Z. Naturf.*, **31a** (1976), 90.
- (6) B. R. Orton, G. K. Malra and A. T. Steel: *J. Phys. F; Met. Phys.*, **17** (1987), L45.
- (7) Y. Kita, M. Zeze and Z. Morita: *Trans. ISIJ*, **22** (1982), 571.
- (8) N. Matsuno, H. Kamiyama, Y. Ishii and M. Momiuchi: *Jpn J. Appl. Phys.*, **25** (1986), 275.
- (9) K. Tuji and K. Yaoita: *Kotai-Buturi*, **24** (1989), 1.
- (10) U. Dahlborg and M. Davidovic: *Phys. Chem. Liq.*, **15** (1986), 243.
- (11) M. Momiuchi: *J. Phys. Soc. Jpn*, **55** (1986), 200.
- (12) H. Richter and G. Breitling: *Adv. Phys.*, **16** (1968), 293.
- (13) J. M. Prober and J. M. Schultz: *J. Appl. Cryst.*, **8** (1975), 405.
- (14) K. Nishikawa and T. Iijima: *Bull. Chem. Soc. Jpn*, **57** (1984), 1750.
- (15) J. Krough-Moe: *Acta Cryst.*, **9** (1956), 351.
- (16) N. Norman: *Acta Cryst.*, **10** (1957), 370.
- (17) H. A. Levy, M. D. Danford and A. H. Narten: ORNL-3960, July, 1966.
- (18) E. Mathiak, W. Nistler, W. Waschkowski and L. Koester: *Z. Metallk.*, **74** (1983), 793.
- (19) T. Iida and R. I. L. Guthrie: *the Physical Properties of Liquid Metals*, Clarendon Press, Oxford, (1988), 30.
- (20) Y. Marcus: *Introduction to Liquid State Chemistry*, John Wiley & Sons Ltd. (1977).
- (21) T. Egami and V. Vitek: *Amorphous Materials: Modeling of structure and Properties*, ed. by V. Vitek, The Metallurgical Society of AIME, (1983), p. 127.
- (22) N. Morito and T. Egami: *Acta Metall.*, **32** (1984), 603.
- (23) T. Shinohe, S. Ikeda, N. Niimura and Y. Ishikawa: *Research Report of Laboratory of Nuclear Science, Tohoku University*, **13** (1980), 95.
- (24) C. B. Gautier, B. C. Giessen and N. J. Grant: *J. Chem. Phys.*, **48** (1968), 1905.
- (25) A. R. Ubbelohde: *Melting and crystal structure*, Clarendon Press, Oxford, (1965).
- (26) M. R. Hoare: *Adv. Chem. Phys.*, **40** (1979), 49.
- (27) S. Saito, S. Ohnishi and S. Sugano: *Phys. Rev. B*, **33** (1986), 7036.