

REACTION MILLED AND SPARK PLASMA SINTERED Al-AIB₂ COMPOSITE MATERIALS

Masahiro Kubota and Makoto Sugamata

¹ Department of Mechanical Engineering, College of Industrial Technology, Nihon University, Narashino, Chiba, Japan

Received: March 29, 2008

Abstract. Air-atomized pure aluminium powder with additions of AIB₂ (Al_{100-x}(AIB₂)_x; x=15, 30, 50) was mechanically alloyed (MA) by using a vibrational ball mill, and MA powders were consolidated by spark plasma sintering (SPS) process. Mechanochemical reactions among pure Al, AIB₂ and stearic acid added as a process control agent (PCA) during MA process and subsequent heat treatments were investigated by X-ray diffraction. The hardness of MA powders under various heat treatment conditions was measured. The mechanical properties of the SPS materials were evaluated through hardness and compression tests. Mechanochemical reactions occurred between the MA powders and PCA after heating from 673 to 873K for 24h. Formation of ternary Al₃BC compound and γ -Al₂O₃ was observed in the Al-AIB₂ MA-powders. The hardness of MA powders was increased dramatically after 4h milling time, and a steady increase was observed up to 64h. The Al₅₀(AIB₂)₅₀ powder after 64h milling time reached a hardness value above HV400. No significant softening was observed in the MA powders after heating from 573 to 873K for 24h. Full density was obtained for the SPS materials, processed from 4h or 8h MA powders of Al₈₅(AIB₂)₁₅, under the SPS conditions of an applied pressure of 49 MPa at 873K for 1h. The compressive proof strength at room temperature of the Al₈₅(AIB₂)₁₅ alloy prepared from the MA4h and MA8h powders was 520 MPa and 620 MPa, respectively.

1. INTRODUCTION

The technique of mechanochemical synthesis (i.e. Reaction milling (RM) [1]) has attracted considerable interest due to the unique material structures [2] and properties [3] that can be developed. In this process, thermodynamically unstable ceramics powders are decomposed by solid-state reactions with the matrix after heat treatment of MA powders. Consequently, *in situ* formation of stable dispersoids may be achieved.

Aluminium-based particulate composite materials fabricated from MA or RM powders and subsequent hot extrusion has been exhibited to desirable mechanical properties at room and elevated temperatures [4]. The microstructures that are formed by the MA or RM processes contain nano-

sized particles, uniformly dispersed in a work hardened, fine grained Al matrix [4]. Various dispersion strengthened aluminium composites have been experimentally developed for applications in structural components by applying the MA or RM processes [3-5].

Spark plasma sintering (SPS) is a novel technique developed for sintering advanced ceramics and composite materials. The advantage of the SPS process is that it allows fabrication of bulk materials from powders using relatively short sintering times at low temperatures. Therefore, coarsening of fine grains and nano-sized dispersed particles in MA powders can be avoided, and superior mechanical properties can be achieved compared to that of materials produced by general powder metallurgy (P/M) routes [3].

Corresponding author: Masahiro Kubota, e-mail: kubota@cit.nihon-u.ac.jp

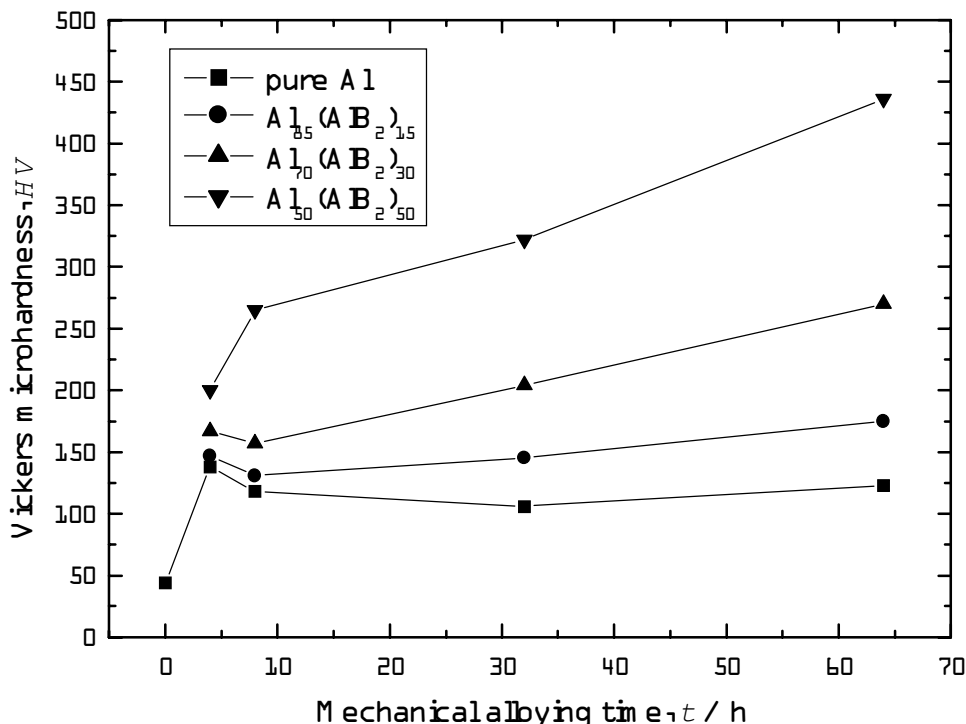


Fig. 1. Change in Vickers microhardness of Al-AIB₂ and pure Al powders with mechanical alloying time.

Table 1. Test materials and designations (at.%).

Materials (at.%)	Designation
Al-15AlB ₂	Al ₈₅ (AlB ₂) ₁₅
Al-30AlB ₂	Al ₇₀ (AlB ₂) ₃₀
Al-50AlB ₂	Al ₅₀ (AlB ₂) ₅₀
pure Al	pure Al

In the present work, pure aluminium powder was mechanically alloyed with AlB₂ powder, and solid-state reactions between these MA powders was induced by various heat treatments. Thus, characteristics of the MA powders, such as mechanical properties and solid-state reaction, were clarified. In addition, mechanical properties of SPS materials fabricated from MA powders were investigated.

2. EXPERIMENTAL PROCEDURES

Mixtures of commercially available 99.9% pure Al powders and 99% pure AlB₂ with average diam-

eters of 100 μm and 74 μm, respectively, were mechanically alloyed. The composition and designation of the experimental materials are listed in Table 1 (at.%). Stainless steel balls of 7 mm in diameter together with 10 g of the Al-AIB₂ (Al_{100-x}(AlB₂)_x where X=15, 30 or 50) powder mixture and stearic acid of 0.25 g as a process control agent were sealed in a hardened steel vial using a glove box filled with argon. The ball to powder mass ratio was approximately 7:1. The MA process was performed at room temperature using an SPEX8000 mixer/mill. The MA processing time was varied from 4 h to 64 h.

The MA powders were heat treated at temperatures from 573 K to 873K for 24 h in air. XRD analysis was performed on both the MA powders and SPS materials using a CuKα radiation source, operating at 40 mA and 60 kV. The average Vickers hardness of the MA powders was determined from 15 particles per sample with a microhardness tester using an applied load of 0.098 N. The MA powders for hardness measurements were mounted into plastic resin, then mechanical grinding with progressively finer SiC papers. Final polishing was

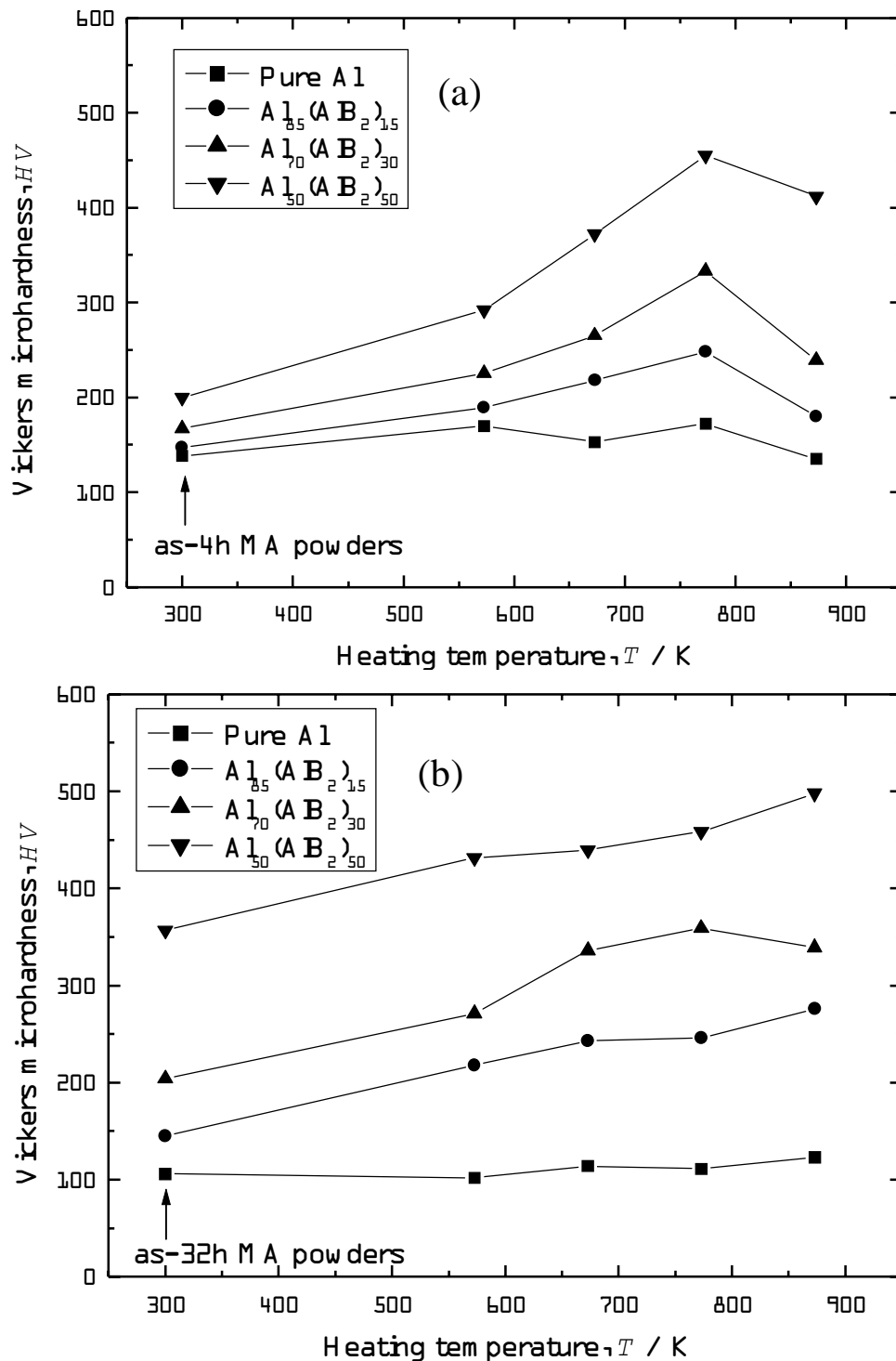


Fig. 2. Change in Vickers microhardness of Al-AlB₂ and pure Al powders after (a) 4 h and (b) 32 h of MA as a function of heat treatment temperature. All samples were heated for 24h in air.

performed with alumina pastes of particle sizes ranging from 0.3 to 0.05 μm .

The MA powders were consolidated by SPS. 7 g of MA powder was placed into a graphite die

Table 2. Hardness and density of SPS-treated materials.

Materials, (at.%)	MA time, (h)	SPS (HV)	Density, (g/cm ³)	Theoretical density, (g/cm ³)	Relative density, (%)
Pure Al	0	39	2.6891	2.699	99.6
	4	139	2.7488		101.8
	8	158	2.7599		102.3
	32	143	2.7249		101
	64	180	2.7834		103.1
Al-15AlB ₂	4	178	2.7569	2.7443	100.5
	8	187	2.7898		101.7
	32	176	2.6944		98.2
	64	147	2.505		91.3
Al-30AlB ₂	4	202	2.8216	2.7598	100.9
	8	189	2.7194		97.3
Al-50AlB ₂	4	109	2.4366	2.8764	84.7
	8	100	2.3773		82.6

of 20 mm in diameter and heated under vacuum with an applied pressure of 49 MPa at 873K for 1 h. The sintering process time was selected for 1 h in order to obtain full bulk density. The Vickers hardness of the SPS materials was measured using an applied load of 9.8 N. The density of the SPS materials was determined using Archimedes' principle.

3. RESULTS AND DISCUSSION

Fig. 1 presents the change in Vickers microhardness of the Al-AlB₂ powders as a function of MA processing time, where pure Al powder is included for reference. The hardness of pure Al powder before MA was approximately HV44. The hardness of the Al₈₅(AlB₂)₁₅ powder increased dramatically to over HV125 after 4 h of MA, and a steady but light increase was observed to less than HV150 after 64 h of MA. The Al₅₀(AlB₂)₅₀ powder exhibited a hardness greater than HV400 after 64 h of MA. These hardness increases can be attributable to the obtained fine crystalline grains, uniform distribution of AlB₂ particles and / or a high density of defects in the matrix manifest by the significant broadening and reduction in the X-ray diffraction peaks with increasing MA times [6]. Further research works to clarify above mentioned should be carried out.

Fig. 2 shows the change in the Vickers microhardness of the MA powders after (a) 4 h and (b) 32 h of MA and heating at temperatures from

573 to 873K for 24 h. In general for all analysed compositions, the Vickers microhardness of the powder after 4 h of MA increased gradually between the heat treatment temperatures of 573K and 673K, reaching its maximum at 773K. However, the Vickers microhardness decreased after heat treatment at 873K. It is assumed that products from solid-state reactions may be attributable for this hardness trend. The further experimental works, however, should be carried out to clarify the reasons of this hardness trend. In contrast, no significant decrease in the Vickers microhardness was observed after 32 h of MA after heating at 873K for 24 h. Similar trends in the hardness as a function of heat treatment temperature were observed for all of the compositions.

X-ray diffraction patterns of the MA powders after (a-b) 4 h and (c-d) 32 h of MA and heating at temperatures from 573 to 873K for 24 h are presented in Fig. 3. Diffraction peaks for both Al and AlB₂ [7] were observed in the as-MA Al₈₅(AlB₂)₁₅ (Fig. 3a). No solid-state reaction occurred after heating up to 673K. However, partial decomposition of AlB₂ was observed, and the formation of Al₃BC [8] was observed after heating at 773K. In addition, new diffraction peaks were observed near 2θ = 46 and 67 degrees, which were identified as γ-Al₂O₃ [9]. The intensity of the Al₃BC peaks increased after heating at 873K, suggesting the promotion of a solid-state reaction during heating. Incomplete de-

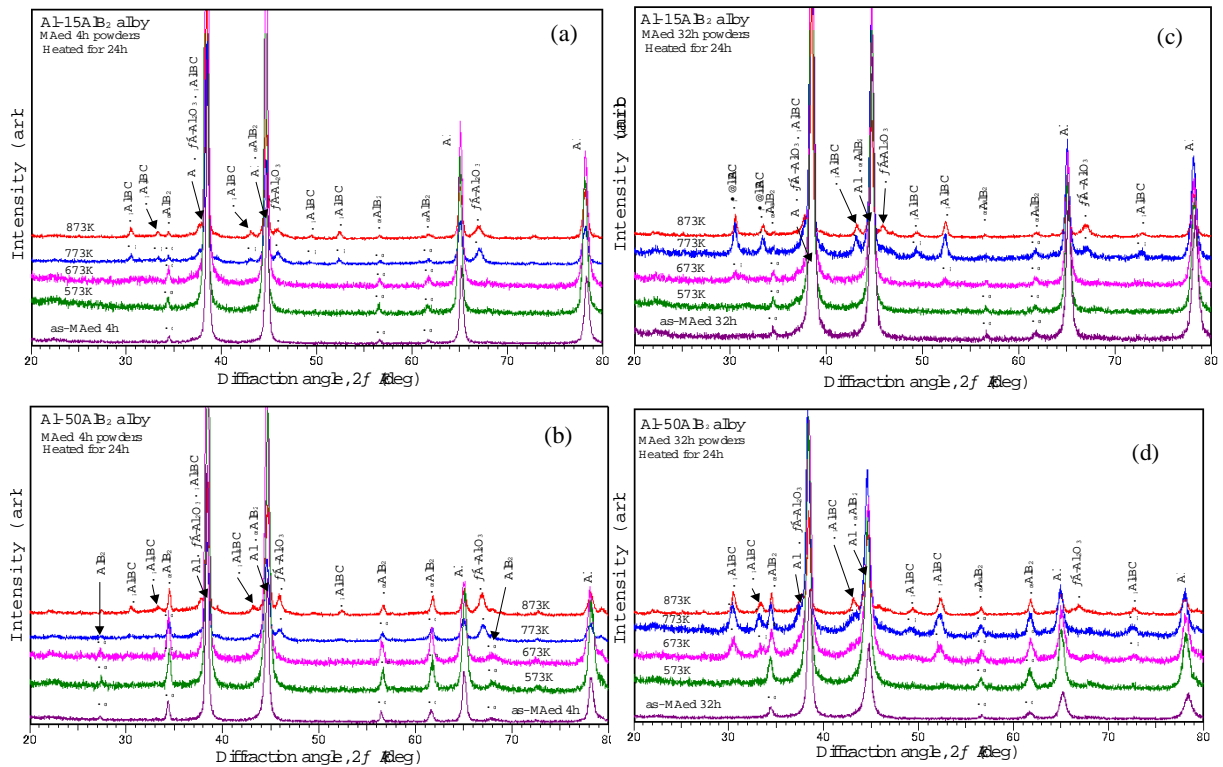


Fig. 3. XRD patterns of MA powders before and after heating at various temperatures for 24 h: (a) Al₈₅(AlB₂)₁₅ 4 h MA, (b) Al₅₀(AlB₂)₅₀ 4 h MA, (c) Al₈₅(AlB₂)₁₅ 32 h MA and (d) Al₅₀(AlB₂)₅₀ 32 h MA.

composition of AlB₂ occurred after heating at 873K. Carbon in the stearic acid (C₁₇H₃₅COOH) might have caused the formation of the ternary Al₃BC compound. In the case of higher AlB₂ contents, such as Al₅₀(AlB₂)₅₀ (Fig. 3b), the formation of Al₃BC occurred after heating at 873K. These results imply that decomposition of AlB₂ occurred at higher heating temperatures as the amount of AlB₂ was increased. The formation of Al₃BC and g-Al₂O₃ is thought to cause an increase in the hardness due to the effect from dispersion hardening of these particles. Even though the MA processing time for Al₈₅(AlB₂)₁₅ and Al₅₀(AlB₂)₅₀ was increased to 32 h, no solid-state reaction was observed after heated up to 573K (Figs. 3c and 3d). However, after heating at 673K, partial decomposition of AlB₂ and formation of Al₃BC was observed. These results suggest that solid-state reaction in MA powders is promoted by lower heat treatment temperatures as the MA processing time increases. Even with increased amounts of AlB₂ and MA processing time, complete decomposition of AlB₂ was not achieved.

Fig. 4 compares the Vickers hardness of the MA powders and bulk materials produced by the SPS process from Al₈₅(AlB₂)₁₅. The hardness values of the SPS materials produced from 4 h, 8 h, and 32 h MA powders were higher than that of the MA powders, but lower than that of the 64 h MA powder. As presented in Table 2, if relative density is approaching to 100%, the hardness value of the SPS materials shows higher than that of MA powder. These results indicate that the SPS process was beneficial for the consolidation of the bulk materials, and the selected conditions for the SPS process in the current research except for 64 h were optimal for the MA powders used.

The relationship between the hardness and density obtained from measurements of the SPS materials together with theoretical values of density is presented in Table 2. In this calculation, no consideration for the value of the elemental density of solid - state reaction products and impurities was made. The SPS materials produced from 4 h and 8 h MA powders revealed a relative den-

Table 3. 0.2% compressive proof stress at room temperature for SPS materials together with the hardness values.

material	0.2% compressive stress (MPa)	HV	σ_y/HV
Al-15AlB ₂ MA4h SPS	520	178	2.92
Al-15AlB ₂ MA8h SPS	620	187	3.32
pure Al MA0h SPS	173	39	4.43
pure Al MA8h SPS	440	158	2.78
			average 3.36

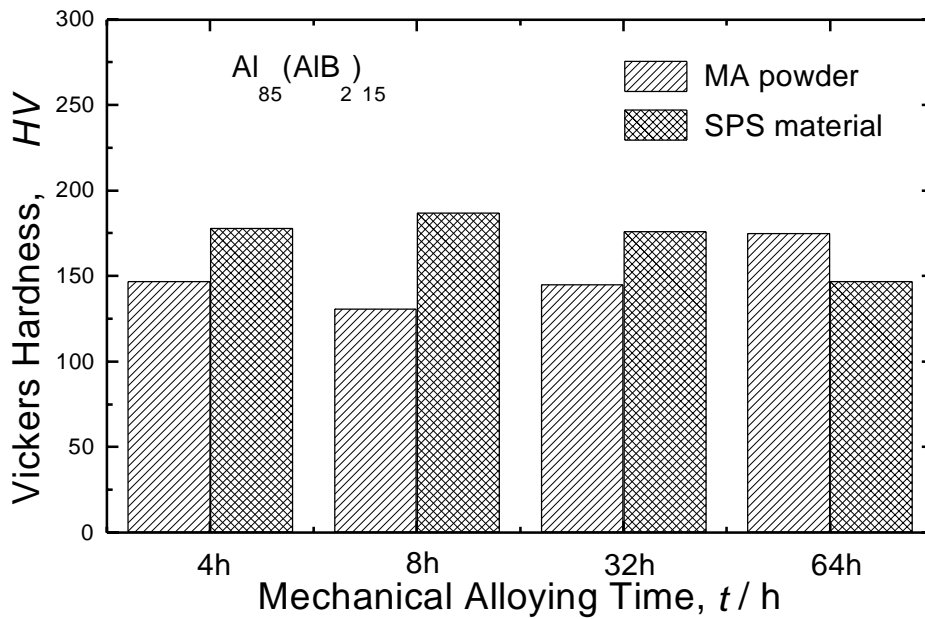


Fig. 4. Comparison of hardness between MA powders and SPS materials of Al₈₅(AlB₂)₁₅.

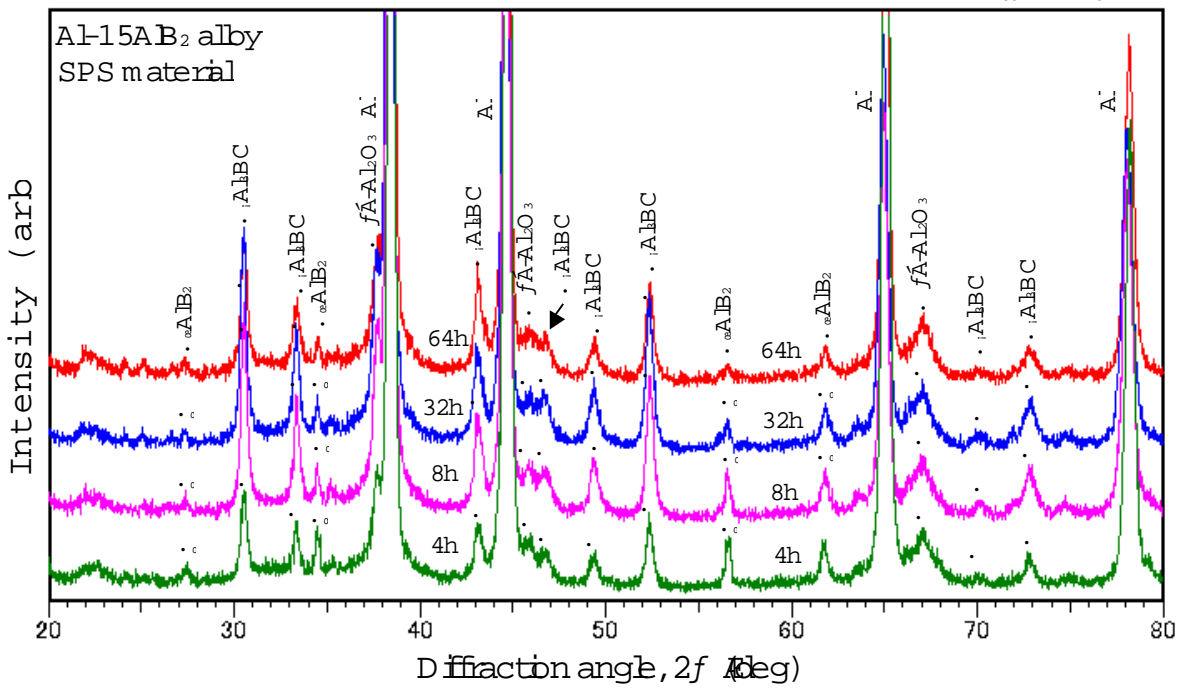


Fig. 5. XRD patterns of the SPS treated Al₈₅(AlB₂)₁₅ alloy, sintered from MA powders after different MA times.

sity greater than 100%. It is presumed that the SPS materials contain intermetallic compounds formed by solid-state reactions during the SPS process and/or due to contamination by Fe originating from the container and balls during MA. However, the relative density of the SPS materials decreased when increasing the amounts of AIB₂ and MA time.

Fig. 5 shows the X-ray diffraction patterns of Al₈₅(AIB₂)₁₅ SPS-materials. The products of solid-state reactions, such as Al₃BC and γ -Al₂O₃, were formed during the SPS process and complete decomposition of the added AIB₂ did not occur. This result is similar to that of the heat treated MA powders as shown in Fig. 3. Therefore it clearly implies that solid-state reactions during SPS can be predicted based on analysing of solid-state reactions of the MA powders.

The value of the 0.2% compressive proof stress for the SPS materials (also from pure Al powder) are shown in Table 3. The compressive proof stress of the Al-AIB₂-based SPS materials was approximately 1.4 times higher than that of the pure Al SPS material, e. g. 620MPa for Al₈₅(AIB₂)₁₅ MA8 h, 440MPa for pure Al MA8 h. The Al₈₅(AIB₂)₁₅-based SPS material using 8 h MA powder showed the highest compressive proof stress of 620 MPa. Compressive proof stress for the Al₈₅(AIB₂)₁₅-based SPS material using 32 h MA powder was not measured due to difficulties of obtaining specimens for compression tests.

The following relationship (Eq. (1)) between the tensile proof stress and hardness of mechanically alloyed Al alloys at room temperature has been proposed [10]:

$$\sigma_{ty} = HV \times 2.90, \quad (1)$$

where *HV* is the Vickers hardness and σ_{ty} is the tensile proof stress (MPa). From the present research, Eq. (2) was derived from the values of Vickers hardness and 0.2% compressive proof stress of the SPS materials as shown in Tables 2 and 3.

$$\sigma_{cy} = HV \times 3.36, \quad (2)$$

where σ_{cy} is the 0.2% compressive proof stress (MPa). The coefficients in these two equations are approximately equal. Thus, it can be implied that the tensile proof stress of SPS materials may be estimated from either the 0.2% compressive proof stress or the Vickers hardness at room tempera-

ture. It should be noted that this estimation could be useful for SPS materials usually characterised by small specimen dimensions due to limitation of die sizes. Therefore, the tensile tests with standard specimen dimensions cannot be carried out.

4. CONCLUSIONS

The formation of Al₃BC occurred by solid-state reaction between AIB₂ and stearic acid in the MA powders during heating. Incomplete decomposition of AIB₂ was observed even after heating the MA powders at 873K for 24 h. The formation of γ -Al₂O₃ occurred after heating the MA powders at 773K for 24 h. A higher heat treatment temperature was needed to promote solid-state reaction for powders with a higher AIB₂ content. In contrast, for a given composition, solid-state reaction occurred at relatively lower heating temperatures when the MA time was increased. Full densification was obtained in the SPS materials using the 4 h or 8 h MA powders of Al₈₅(AIB₂)₁₅ under an applied pressure of 49 MPa at 873K for 1 h. The SPS materials based on 4 h and 8 h MA Al₈₅(AIB₂)₁₅ exhibited room temperature compressive proof stresses of 520 and 620 MPa, respectively.

REFERENCES

- [1] P. G. McCormick // *Material Transactions, JIM* **36** (1995) 161.
- [2] L. Blaz, J. Kaneko, M. Sugamata and R. Kamei // *Materials Science and Eng. A* **349** (2003) 111.
- [3] M. Tokita // *Mater. Sci. Forum* **308-311** (1999) 83.
- [4] L. Lu and M. O. Lai, *Mechanical Alloying* (Kluwer Academic Publishers, 1998).
- [5] D. G. Kim, J. Kaneko and M. Sugamata // *Materials Transactions, JIM* **36** (1995) 305.
- [6] B.D. Cullity, *Elements of X-ray Diffraction, 2nd ed.* (Addison-Wesley, Reading, 1978).
- [7] PDF:39-1483, *International Centre for Diffraction Data*, 1999.
- [8] PDF:47-1628, *International Centre for Diffraction Data*, 1999.
- [9] PDF:10-0425, *International Centre for Diffraction Data*, 1999.
- [10] J. A. Hawk, R. E. Franck and H. G. F. Wilsdorf // *Metallurgical Transactions* **19A** (1988) 2363.